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SOME GERMANIUM, TIN, AND ALLYL DERIVATIVES OF TRANSITION METALS

by

© DENNIS FREDERICK DONG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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OF DOCTOR OF PHILOSOPHY

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THE UNIVERSITY OF ALBERTA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled

SOME GERMANIUM, TIN, AND ALLYL
DERIVATIVES OF TRANSITION METALS

submitted by Dennis Frederick Dong, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A number of germanium and tin transition metal carbonyl derivatives have been synthesized by thermal and photochemical means from the main group IV hydrides. The infrared, nmr and mass spectral properties were studied and revealed various structural and bonding aspects of these complexes.

The reactions of $PhGeH_3$, R_2GeH_2, and Ph_3GeH ($Ph = C_6H_5$, $R = C_6H_5$ or C_2H_5) with the three binary carbonyls of iron yielded metal-metal bonded compounds such as $(RGe)_2Fe_3(CO)_9$, $[R_2GeFe(CO)_4]_2$, $(R_2Ge)_2Fe_2(CO)_7$, $(R_2Ge)Fe_2(CO)_8$, $(R_2Ge)_3Fe_2(CO)_6$, and $GeFe_4(CO)_{16}$. The thermal decomposition of $(Ph_2Ge)_2Fe_2(CO)_7$ led to the isolation of $[(Ph_2Ge)_2O]Fe_2(CO)_8$, in which the germanium-bonded oxygen atom is believed to be originally from a carbonyl ligand. The novel germoxane compound contains a five-membered heterocycle consisting of the digermoxane linkage and two iron atoms.

A variety of derivatives of $CpM(CO)_3$ ($Cp = \eta-C_5H_5$, M = Mn, Re) has been prepared from the parent tricarbonyls or from the anions, $CpM(CO)_2M'X_3^-$ (M' = Ge, Sn; X = Cl, Br). These complexes are of the type $CpM(CO)_2(M'X_3)Y$, (Y = H, Cl, Br, I, $M'X_3$, CH_3, or C_2H_5), where Y is bonded to the transition metal *trans* to the $M'X_3$ group. Other complexes of the form *trans*-$CpM(CO)_2(M'Ph_3)_2$ and *trans*-$CpRe(CO)_2[Ge(OR)Cl_2]Cl$ ($R = CH_3, C_2H_5$) were also prepared. An unusual reaction involving $CpM(CO)_2M'X_3^-$ and methyl fluorosulphonate led to the formation of the sulphur dioxide complexes $CpM(CO)_2SO_2$.

A number of π-allyl complexes of the form Cp(π-allyl)Re(CO)X (X = H, Cl, Br) were synthesized. The proton nmr spectra indicate highly inequivalent environments for the *syn* and *anti* protons on the π-allyl ligand. Arguments based on chemical shifts, coupling constants, and decoupling experiments were used to assign the resonances. The preparation and proton nmr spectrum of (π-1-methylallyl)$Fe(CO)_3GeCl_3$ are also described.

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CHAPTER I

GENERAL ASPECTS OF TRANSITION METAL CARBONYL COMPLEXES

The chemistry of transition metal carbonyl complexes has become a very large field of study since its sudden growth beginning in the mid-1950's. Although transition metal carbonyls have been known since the discovery of $Ni(CO)_4$ in 1897[1], a systematic investigation of their chemistry did not start until recent years. Indeed, the synthesis of a complete series of main group IV* metal-transition metal carbonyl compounds did not occur until after 1960. With the vast increase in the number of publications in organo-transition metal chemistry, a guide to the literature covering the years 1950-1970 appeared in 1972.[2] This comprehensive guide lists text-books and conference reports, as well as journals and abstracts covering organo-transition metal chemistry. More recent publications include the second volume of the "Specialist Periodical Report" on "Organometallic Chemistry"[3] and the M.T.P. International Review of Science, Series One, on inorganic chemistry.[4] A number of review articles covering specifically main group IV-transition metal carbonyl compounds has appeared since the beginning

*Hereafter, "group IV metals" shall refer to the main group elements silicon, germanium, tin, and lead, even though silicon is not usually classed as a metal.

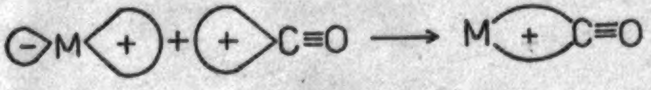
of 1970.[5-7] Also of note are the annual surveys and subject reviews appearing in such publications as the "Journal of Organometallic Chemistry" and "Advances in Organometallic Chemistry", among many others.

The growth in transition metal carbonyl chemistry can probably be attributed to a number of causes: the use of these compounds as homogeneous and heterogeneous catalysts in industrial processes, the study of these compounds as model systems for simple metallic behavior, and the increasing availability of transition metal compounds as starting materials. A secondary reason related to the first two is the detailed study of metal to ligand bonding in metal complexes, in view of the diverse nature of such modes of bonding. Convenient sources of all transition metal carbonyls for use as starting materials now exist. There are also many improved methods for obtaining silicon, germanium, tin, and lead compounds for reactions with transition metal carbonyls, as well as new methods of carrying out such reactions.[8]

The following sections of this chapter will deal with, first, the nature of bonding and structure in transition metal carbonyl complexes; secondly, a summary of synthetic methods for the preparation of metal carbonyl derivatives; and lastly, a discussion of the spectrometric methods employed in the study of these compounds.

A SIMPLIFIED VIEW OF BONDING AND STRUCTURE IN METAL CARBONYL COMPLEXES

The existence of transition metal carbonyl complexes is generally accepted as being related to the stabilization of the metal in a low formal oxidation state. This stabilization is accomplished by bonding to such ligands as tertiary phosphines, nitric oxide, and various cyclic olefins, as well as carbon monoxide. The strong metal-ligand bonds in these complexes are generally attributed to the synergic effect of σ and π interactions.[9,10] A simplified molecular orbital picture of this effect for a carbonyl ligand is shown in 1 and 2. A metal-carbon σ bond is formed by overlap of a filled sp-hybrid orbital of carbon and a vacant hybrid orbital of the metal in 1. Back donation to form π bonds is accomplished by overlap of filled d orbitals of the metal with empty antibonding π^* orbitals of CO in 2. The π bonding serves to remove excess negative charge built up on the metal atom by σ donation.



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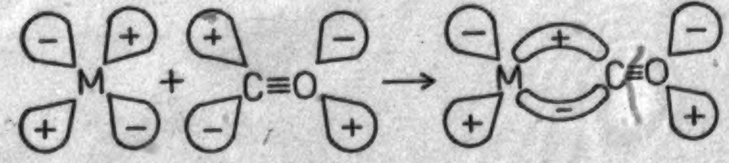

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A major consequence of this synergic electron transfer process is the reduction of the CO bond order by the increase in electron density in the π^* antibonding orbital of CO. A manifestation of this change is evident from infrared spectroscopy, where the stretching frequency of free CO occurs about 2155 cm^{-1}, whereas ν(CO) is lowered, usually below 2100 cm^{-1}, in transition metal carbonyl complexes.

Numerous attempts have been made to estimate the relative contributions of the σ-donor and π-acceptor properties of various ligands to the transition metal-ligand bond. These studies have been carried out mainly through the use of infrared spectroscopy,[11,12] although other approaches have been made.[13] It now seems that, since donor and acceptor properties are mutually supportive, predictions of the chemical and physical properties of these low-valent metal complexes must take into account both σ and π properties of the ligand, and possibly also all the competing ligands in the complex.

The number and type of ligands in a transition metal carbonyl complex can usually be rationalised by invoking the effective atomic number rule, also known as the "noble gas formalism".[14] This formalism requires that the number of electrons possessed by the transition metal plus the number of electrons contributed by the ligands equals the number of electrons in the succeeding noble gas atom. The implication is that the valence shell, and specifically the d orbitals, of the transition metal will be completely filled. Ligands such as carbon monoxide and tertiary phosphines are considered to be two electron donors. Covalent single bonds to other metals, hydrogen, halogens, and alkyl groups are all considered to involve one electron donors. The nitrosyl group, and halogen atoms bridging two metal atoms, donate three electrons to the metal system. The π-bonded benzene, cyclopentadienyl, cyclobutadienyl, allyl, and ethylenic groups supply six, five, four, three, and two electrons respectively.

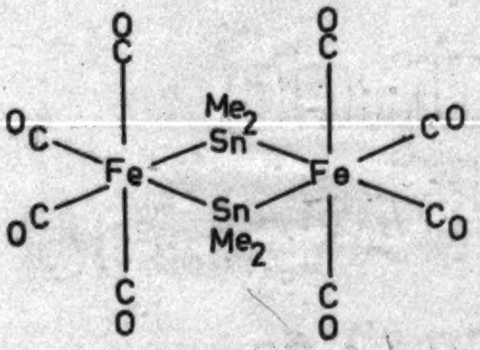
Although a number of transition metal complexes do not conform to the effective atomic number rule, notably many of rhodium, iridium, palladium, and platinum, the vast majority of such complexes do conform, and the usefulness of this rule for predicting stoichiometries and possible structures of compounds cannot be understated.

As an illustration of the noble gas formalism, the compound CpRe(CO)(NO)H*[15] contains a rhenium atom which requires eleven electrons from the ligands to attain the electronic configuration of the next noble gas, radon. These electrons are supplied as follows: five from the cyclopentadienyl ring, three from the nitrosyl ligand, two from the carbonyl, and one from the hydrogen atom.

---

*Throughout this work the following abbreviations will be employed: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, Cp = η-C_5H_5, and THF = tetrahydrofuran.

The compound, $[Me_2SnFe(CO)_4]_2$, whose empirical formula suggests an improbable stannylene-type structure, would require at least a dimeric formulation when applying the effective atomic number rule to obtain a logical structure. Indeed, an X-ray crystallographic study[16] has shown structure 3 to be the case, in which each iron atom obtains its effective atomic number of electrons, and each tin atom remains tetravalent.



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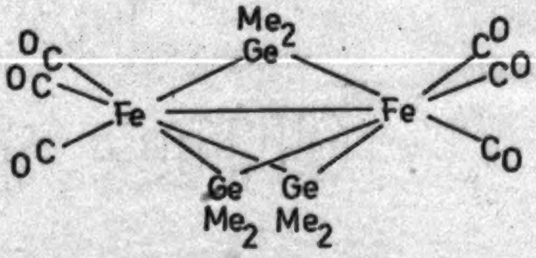

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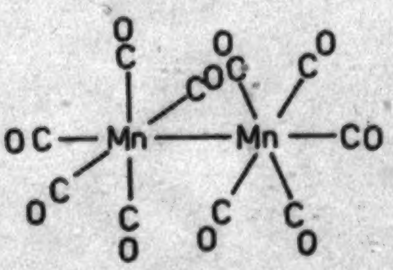
A comparison between 3 and 4 would reveal that for the effective atomic number rule to hold, an iron-iron bond is not required in 3, but would be in 4, since each iron atom requires ten electrons from the ligands. The X-ray crystal structures support this contention. The iron-iron distance in $(Me_2Ge)_3Fe_2(CO)_6$ is 2.750(11) Å,[17] while that in $[Me_2SnFe(CO)_4]_2$ is 4.14 Å.[16] As a second comparison with 4, the corresponding distance in $[Cl_2SiFe(CO)_4]_2$, analogous to 3, is 3.76 Å.[18] The distance reported for 4 is in good agreement with twice the estimated single bond covalent radius for iron (1.34 Å).[19] It should be noted here that bond distances estimated from covalent radii do vary depending on bridging groups across the metal-metal vector, but certainly can be used to ascertain the presence or absence of a metal-metal bond.

Although the existence of metal-metal bonds is now generally accepted, it was not until 1957 that the unambiguous existence of covalent bonds between transition metals was first demonstrated. Dahl, Ishishi, and Rundle,[20] with the structural determination of $Mn_2(CO)_{10}$, 5, and Wilson and Shoemaker,[21] with that of $[CpMo(CO)_3]_2$, 6, showed that the compounds possess no bridging ligands, and the two symmetric halves are held together only by metal-metal bonds.



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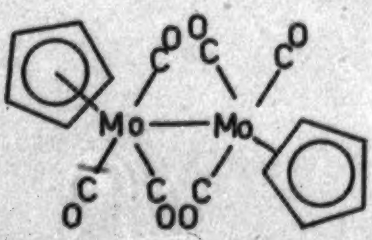


6

SYNTHETIC METHODS

There have been several publications that include summaries of the synthetic methods used in the chemistry of transition metal carbonyls and their derivatives.[5,22-24] A comprehensive survey of photochemical reactions of metal carbonyl compounds appeared in 1969.[25] In view of the variety of methods used successfully in the preparation of compounds in this work, a full discussion of these methods will be given here.

The reactions employed in the synthesis of metal carbonyl complexes can usually be placed in one of several general categories:

1. Displacements of halide ions by metal carbonyl anions.
2. Oxidative additions and oxidative eliminations.
3. Eliminations of neutral molecules.
4. Insertion reactions.
5. Miscellaneous reactions.

Some reactions can be placed under more than one category and in these cases the choice has been arbitrary. The classification of the reactions has no mechanistic implications and is based solely on the net results of the reactions. Although most of these reactions are applicable to main group metals in general, the examples given will stress their usage for the formation of group IV metal-transition metal compounds, since these form the bulk of the complexes in this work. Examples of reactions with other main group elements will be given only in cases where they are relevant to compounds in this thesis.

1. Displacement of halide ions by metal carbonyl anions.

This method has been applied extensively to compounds of the chromium, manganese, iron, and cobalt groups, since the preparation of carbonyl anions of these metals is relatively straightforward.[24,26,27] This is probably the most widely used method for the preparation of group IV metal-transition metal bonds:

$$CpW(CO)_3^- + Ph_3GeBr \rightarrow CpW(CO)_3GePh_3 + Br^- \qquad [28]\ (\text{I-1})$$

$$Mn(CO)_5^- + GeCl_4 \rightarrow Mn(CO)_5GeCl_3 + Cl^- \qquad [29]\ (\text{I-2})$$

$$4CpFe(CO)_2^- + SnCl_4 \rightarrow [CpFe(CO)_2]_4Sn + 4Cl^- \qquad [30]\ (\text{I-3})$$

$$2Co(CO)_4^- + Ph_2PbCl_2 \rightarrow [Co(CO)_4]_2PbPh_2 + 2Cl^- \qquad [31]\ (\text{I-4})$$

$$2Ir(CO)_3(Ph_3P)^- + Me_2SnCl_2 \rightarrow [Ir(CO)_3(Ph_3P)]_2SnMe_2 + 2Cl^- \qquad [32]\ (\text{I-5})$$

$$2Os(CO)_4^{=} + 2Ph_2SnCl_2 \rightarrow [Ph_2SnOs(CO)_4]_2 + 4Cl^- \qquad [33]\ (\text{I-6})$$

$$Co(CO)_4^- + H_3SiI \rightarrow Co(CO)_4SiH_3 + I^- \qquad [34]\ (\text{I-7})$$

Applications of this method in this work will be seen mainly in Chapter III.

2. Oxidative addition and oxidative elimination reactions.

Essentially both of these types of reaction are similar, since the coordination number and formal oxidation state of the transition metal are increased. The formal oxidation state of a metal atom may be obtained by removing all ligands in their closed shell configurations, i.e. with their bonding orbitals electronically filled. Therefore saturated alkyl and main group IV ligands, halogens, and hydrogen atoms are removed as mono-anions. Carbonyl, nitrosyl, and phosphine ligands are removed as neutral molecules. The oxidation states of the central metal atoms in $Mn(CO)_5^-$, $Cr(CO)_5PPh_3$, $Cl_3GeCo(CO)_4$, and $CpFe(CO)_2SiMe_3$, are -I, 0, I, and II, respectively.

In oxidative addition reactions two one-electron donor ligands, usually from the same molecule, are added to an electronically unsaturated (i.e., short of the effective atomic number of electrons) transition metal, and the coordination number is increased by two. In oxidative elimination reactions a two-electron donor ligand on the metal is displaced by the addition of two one-electron donor ligands, and the coordination number is increased by one. This method is especially suitable in metal carbonyl chemistry, since the ejected CO molecule is easily removed from the reaction mixture as a gas, ensuring a non-equilibrium reaction. Some examples of oxidative addition and elimination reactions are:

$(Ph_3P)_2Rh(CO)Cl + HSiCl_3 \rightarrow (Ph_3P)_2Rh(CO)Cl(SiCl_3)H$[35] (I-8)

$(Ph_3P)_2Ir(CO)I + HSnPh_3 \rightarrow (Ph_3P)_2Ir(CO)(I)(SnPh_3)H$[36] (I-9)

$(Ph_3P)_3Ir(CO)H + HSi(OEt)_3 \rightarrow (Ph_3P)_2Ir(CO)H_2$-$[Si(OEt)_3] + Ph_3P$ [37] (I-10)

$(bipyridyl)Mo(CO)_4 + GeCl_4 \rightarrow (bipyridyl)Mo(CO)_3$-$Cl(GeCl_3) + CO$ [38] (I-11)

$Re_2(CO)_{10} + Ph_2SiH_2 \rightarrow Re_2(CO)_8Ph_2SiH_2 + 2CO$ [39] (I-12)

$Fe(CO)_5 + SnI_4 \rightarrow Fe(CO)_4I(SnI_3) + CO$ [40] (I-13)

$CpCo(CO)_2 + HSiCl_3 \rightarrow CpCo(CO)H(SiCl_3)$ [41] (I-14)

3. Elimination of neutral molecules.

Often similar to oxidative elimination, especially when CO is the neutral molecule "eliminated", this method is also often simplified by the ease of removal of one of the products. As can be seen from the examples, the oxidation state of the metal can be increased, or can remain unchanged:

$Fe_3(CO)_{12} + 6HSiCl_3 \rightarrow 3Fe(CO)_4(SiCl_3)_2 + 3H_2$ [42] (I-15)

$Hg[Fe(CO)_2Cp]_2 + SnCl_2 \rightarrow [CpFe(CO)_2]_2SnCl_2 + Hg$ [43] (I-16)

$$Co_2(CO)_8 + Ph_2GeH_2 \rightarrow Ph_2GeCo_2(CO)_7 + H_2 + CO$$ [44] (I-17)

$$Fe(CO)_5 + (Me_3Si)_2Hg \rightarrow Fe(CO)_4(SiMe_3)_2 + Hg + CO$$ [45] (I-18)

$$CpW(CO)_3H + Me_3SnNMe_2 \rightarrow CpW(CO)_3SnMe_3 + HNMe_2$$ [46] (I-19)

$$C_7H_7Mo(CO)_2Cl + HGeCl_3 \rightarrow C_7H_7Mo(CO)_2GeCl_3 + HCl$$ [47] (I-20)

$$ClMn(CO)_5 + HGeCl_3 \rightarrow Mn(CO)_5GeCl_3 + HCl$$ [48] (I-21)

$$Ru_3(CO)_{12} + 3C_3H_5Br \rightarrow 3C_3H_5Ru(CO)_3Br + 3CO$$ [49] (I-22)

$$C_6H_6Cr(CO)_3 + 3SnCl_3^- \rightarrow Cr(CO)_3(SnCl_3)_3^{-3} + C_6H_6$$ [50] (I-23)

The application of this method as a general synthetic route has been explored very widely in the last few years, and is the synthetic method used most often in Chapter II.

4. Insertion Reactions.

This method essentially entails oxidative addition to germanium, tin, or lead dihalides, if a group IV metal-transition metal bond is formed. Since silicon dihalides are not readily available, the formation of silicon-transition metal bonds by this method has not been investigated. The insertion may occur between metal-metal or metal-halogen bonds. Illustrations of some insertion reactions are given below:

$$Cr_2(CO)_{10}^{=} + SnI_2 \rightarrow [Cr(CO)_5]_2SnI_2^{=}$$ [51] (I-24)

$$[CpFe(CO)_2]_2 + GeI_2 \rightarrow [CpFe(CO)_2]_2GeI_2$$ [52] (I-25)

$CpFe(CO)_2Cl + SnCl_2 \rightarrow CpFe(CO)_2SnCl_3$ [53] (I-26)

$Co_2(CO)_8 + SnI_2 \rightarrow [Co(CO)_4]_2SnI_2$ [54] (I-27)

In reactions I-20 and I-21, $HGeCl_3$ is believed to be a source of $GeCl_2$ and HCl, and therefore the reactions may be viewed as insertions of $GeCl_2$. Indeed, considerable evidence now suggests that an equilibrium mixture of di- and tetra-valent germanium exists in solution:

$HGeCl_3 \rightleftarrows H^+GeCl_3^- \rightleftarrows HCl + GeCl_2$ [55-57] (I-28)

Other types of insertion reactions, in which the "inserted" species is not a group IV dihalide, are quite numerous. The reactions most often involve metal-carbon or metal-hydrogen σ bonds and include insertions of such molecules as carbon monoxide, sulphur dioxide, isocyanides, olefins, and acetylenes. A good overview of these reactions, including references to recent review articles, is given in the M.T.P. International Review of Science.[58]

One other type of insertion reaction involves the formation of bonds to two one-electron donors by the reaction with a main group IV anion:

$CpMo(CO)_3CH_3 + GeCl_3^- \rightarrow CpMo(CO)_2(GeCl_3)[C(O)CH_3]^-$ [59]

(I-29)

5. Miscellaneous Reactions.

a) Ligand displacement reactions.

Complexes formed from these reactions are actually derivatives of compounds synthesized by previous methods. However, this class of reactions should be mentioned since new compounds are prepared by this route. There are two forms of these reactions, one in which the oxidation state of the metal remains the same, and one in which it is reduced:

$CpMn(CO)_3 + Ph_3P \rightarrow CpMn(CO)_2Ph_3P + CO$ [60] (I-30)

$C_6H_6Mn(CO)_3^+ + CN^- \rightarrow C_6H_6Mn(CO)_2CN + CO$ [61] (I-31)

$CpMn(CO)_2(Ph_3Si)H + Ph_3P \rightarrow CpMn(CO)_2Ph_3P + HSiPh_3$ [62] (I-32)

The first example (I-30) is one of a very large class of displacement reactions by Lewis bases, and their general nature has been reviewed.[63,64] The last reaction is also termed "reductive elimination" and is, as the name suggests, the opposite of oxidative elimination.

b) Formation of metal-metal bonds by loss of ligands.

This method is a variation of method 3, where the neutral molecule eliminated is initially a discrete ligand on the starting material, and no other reactant is involved. The thermal or photochemical loss of a ligand is accompanied by formation of a metal-metal bond and conversion of a terminal ligand to a bridging position:

$CpFe(CO)_2PPh_2Fe(CO)_4 \rightarrow CpFe(CO)(PPh_2)Fe(CO)_4 + CO$ [65] (I-33)

$Ph_2Ge[Co(CO)_4]_2 \rightarrow Ph_2GeCo_2(CO)_7 + CO$ [44,66] (I-34)

$2Me_2GeClMn(CO)_5 \rightarrow (Me_2Ge)_2Mn_2(CO)_8 + Cl_2 + 2CO$ [67] (I-35)

$Fe(CO)_4AsMe_2W(CO)_3Cp \rightarrow Fe(CO)_4AsMe_2W(CO)_2Cp + CO$ [68] (I-36)

c) Reactions of coordinated ligands.

This preparative method is a member of a very large class of reactions which includes, among others, synthesis of carbene complexes[69,70] and ortho-metallated complexes.[71] In this work, however, reactions of coordinated ligands are restricted to substitutions of atoms or groups of atoms in the ligand itself, with no change in the structural arrangement of the metal complex as a whole. Examples of these reactions usually involve halogen atoms:

$$[CpFe(CO)_2]_2GeCl_2 + 2NaOMe \rightarrow [CpFe(CO)_2]Ge(OMe)_2 + 2NaCl \qquad ^{72}(I\text{-}37)$$

$$CpW(CO)_3SnMe_3 + HCl \rightarrow CpW(CO)_3SnMe_2Cl + CH_4 \qquad ^{73}(I\text{-}38)$$

$$Mn(CO)_5GePh_2Cl + AgBF_4 \rightarrow Mn(CO)_5GePh_2F + AgCl + BF_3 \qquad ^{74}(I\text{-}39)$$

$$Mn(CO)_5SnMe_3 + HSiCl_3 \rightarrow Mn(CO)_5SnMe_2Cl + MeSiCl_2H \qquad ^{75}(I\text{-}40)$$

$$CpNi(PPh_3)GeCl_3 + Et_4Pb \rightarrow CpNi(PPh_3)GeCl_2Et + Et_3PbCl \qquad ^{76}(I\text{-}41)$$

INSTRUMENTAL METHODS

The main spectrometric methods used in the study of transition metal carbonyl complexes are infrared, nuclear magnetic resonance, and mass spectrometry. In a few cases Raman spectroscopy has been used to complement information obtained from infrared spectroscopy.

Absorption bands in the carbonyl stretching region of the infrared spectrum are most useful in monitoring reactions, determining number and purity of products, and assigning possible structures.[77] Usually solution spectra in relatively nonpolar solvents such as saturated hydrocarbons or dichloromethane are measured, although in a few cases solid state spectra are useful.

The narrow line widths and strong intensities of carbonyl stretching bands make them ideal for the study of metal carbonyl complexes when using high resolution spectrometers. Comparison of band positions and relative intensities aids in postulating and eliminating possible reaction products as well as indicating physical and possible chemical differences between similar compounds. As mentioned before, stretching force constants obtained from band positions have been used as a probe of electronic effects in bonding[11,12,78] and reactivity.[79] Attempts have also been made to use infrared intensities to study electronic effects[80,81] and even to calculate bond angles in metal carbonyl derivatives.[11,82,83] One review article on vibrational spectra of carbonyl complexes has proved to be a particularly useful general reference.[84]

Mass spectrometry is usually a definitive method of ascertaining the molecular weight of a compound providing it is sufficiently volatile. As well, isotope combination patterns, exact mass determination and stepwise fragmentation patterns allow one to deduce the elemental composition together with possible structures of the complex. For most neutral compounds with masses as high as 1000 or more, reasonable mass spectra can be obtained, as long as ligands such as tertiary phosphines and arsines, which make the compound involatile, are not present. It has been clearly demonstrated[85,86] that transition metal carbonyl complexes easily lose carbon monoxide in a stepwise fashion in a mass spectrometer. This property often enables one to simply count the number of carbonyl ligands contained in a compound. Other modes of mass spectral cleavage and rearrangement are summarized in a recent review article.[87]

Nuclear magnetic resonance spectroscopy of a variety of nuclei has been used to study transition metal complexes. In this work all magnetic resonance information relevant to the study and characterization of the compounds of interest was obtained using proton magnetic resonance. A number of reviews pertinent to this work has been published.[88-90]

CHAPTER II

SYNTHESIS AND PROPERTIES OF SOME GERMANIUM-IRON CARBONYL COMPOUNDS

INTRODUCTION

Until the early 1970's the number of reported germanium-iron carbonyl compounds was relatively small. Seyferth and coworkers reported the synthesis of the first germanium-iron complex, $CpFe(CO)_2GePh_3$, from $Na[CpFe(CO)_2]$ and Ph_3GeBr in 1962.[91] Most of the other early iron-germanium derivatives contained the $CpFe(CO)_2$ group, bonded to a single germanium atom.

Kahn and Bigorgne reported the synthesis of the first iron complexes containing only CO and germanium bonded to the iron atom: $[(R_2Ge)Fe(CO)_4]_2$ (R = Me, Et) from $Na_2Fe(CO)_4$ and R_2GeCl_2 in 1966[92] and then $(Et_3Ge)_2Fe(CO)_4$ from Et_3GeH and $Fe_3(CO)_{12}$ in 1967.[93] A list of compounds containing iron-germanium bonds, complete up to September, 1974, is given in Table I.

In this department, Dr. E. H. Brooks succeeded in isolating a number of organogermanium-iron complexes from the sealed tube reactions of triiron dodecacarbonyl and diiron enneacarbonyl with R_2GeH_2 (R = Me, Ph): $(Ph_2Ge)_2Fe_2(CO)_7$,[98] **7**, $(Me_2Ge)_3Fe_2(CO)_6$,[17,97] **8**, $Ph_2GeFe_2(CO)_8$, **9**, $[Ph_2GeFe(CO)_4]_2$, **10**, $(Me_2Ge)_2Fe_2(CO)_7$, $(MeGeH)(Me_2Ge)_2Fe_2(CO)_6$, and $(PhGeH)(Ph_2Ge)_2Fe_2(CO)_6$.

TABLE I

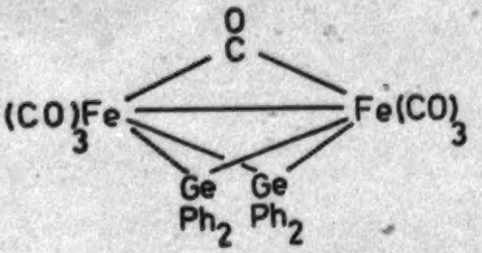
COMPOUNDS CONTAINING IRON-GERMANIUM BONDS

Compound	Abbreviations	References
$GeFe_4(CO)_{16}$		94,95,‡
$(RGe)_2Fe_3(CO)_9$	R = Et, Ph	‡
$[(Ph_2Ge)_2O]Fe_2(CO)_8$		‡
$[R_2GeFe(CO)_4]_2$	R = Me, Et, Ph	92,96,‡
$[X_2GeFe(CO)_4]_2$	X = Cl, Br, I	40
$R_2GeFe_2(CO)_8$	R = Et, Ph	96,97,‡
$(R_2Ge)_2Fe_2(CO)_7$	R = Me, Et, Ph	96,98,‡
$(R_2Ge)_3Fe_2(CO)_6$	R = Me, Et, Ph	17,96,‡
$(RGeH)(R_2Ge)_2Fe_2(CO)_6$	R = Me, Ph	96
$Fe(CO)_4[GePh_2M(CO)_5]_2$	M = Mn, Re	99
$Fe(CO)_4(GeR_3)H$	R = H, Ph	47,100
$Fe(CO)_4(GeI_3)I$		40
$[Et_4N][Fe(CO)_4GePh_3]$		47
$[Ph_4As][Fe(CO)_4GeCl_3]$		101
$Fe(CO)_4(GeR_3)_2$	R = H, Et	93,100,102
$Fe(CO)_4(GeX_3)_2$	X = Cl, Br, I	40
$Fe(CO)_4(GeCl_2)_2[CpCo(CO)]_2$		103,104
$(\eta\text{-}C_3H_5)Fe(CO)_3GeR_3$	R = Me, Ph	105
$(\eta\text{-}C_3H_5)Fe(CO)_3GeR_2Cl$	R = Me, Ph	105
$(\eta\text{-}C_3H_5)Fe(CO)_3GeRCl_2$	R = Me, Ph	105
$(\eta\text{-}C_3H_5)Fe(CO)_3GeX_3$	X = Cl, Br	105
$(1\text{-}3\text{-}\eta\text{-}1\text{-}MeC_3H_4)Fe(CO)_3GeCl_3$		‡

TABLE I (continued)

Compound	Abbreviations	References
$[(\eta\text{-}C_3H_5)Fe(CO)_3]_2GeBr_2$		105
$Fe(CO)_2L(NO)GePh_3$	L = CO, $P(OPh)_3$	106
$Fe(CO)_3(NO)Ge(C_2H_3)Me_2$		107
$Fe(CO)_2(NO)(Cl)Ge(C_2H_3)Cl$		108
$Fe(CO)_2(NO)(X)GeMe_2$	X = Cl, Br	108
$CpFe(CO)_2GeR_3$	R = H, Me, Et, Ph, OMe, $MeCO_2$	91,100,109, 110
$CpFe(CO)_2GeMe_2R$	R = C_2H_3, Cl	67,107
$CpFe(CO)_2GeMeX_2$	X = Cl, Br, I	111
$CpFe(CO)_2GeRCl_2$	R = Me, Et, C_3H_7	111,112
$CpFe(CO)_2GeX_3$	X = F, Cl, Br, I	110,113
$[CpFe(CO)_2]_2GeR_2$	R = H, Me, Et, Ph, OMe, C_3H_5, C_4H_9, C_5H_5, SEt, NCS, $MeCO_2$	52,72
$[CpFe(CO)_2]_2GeX_2$	X = F, Cl, Br, I	52,72,113
$[CpFe(CO)GeR_2]_2$	R = Me, Ph	67,114
$[CpFe(CO)]_2(CO)GeR_2$	R = Me, Ph	66,67
$[CpFe(CO)_2GeR_2]_2$	R = Me, Et	109
$CpFe(CO)_2(GeX_2)Ni(CO)Cp$	X = Cl, Br	115
$Cp(C_4H_6)FeGeCl_2Me$		116
$[CpFe(CO)_2GeMe_2]_2O$		117

‡ Compound prepared in this work.



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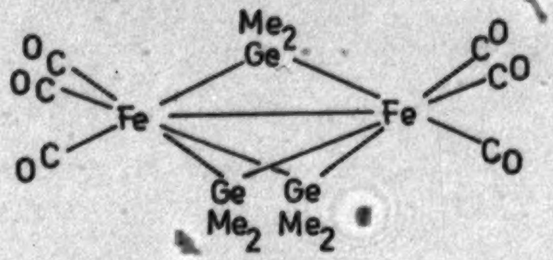

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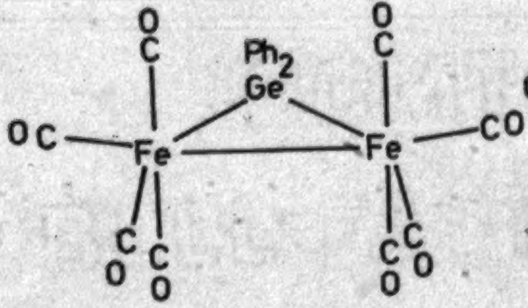

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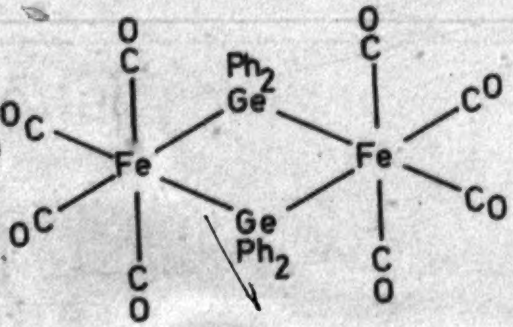

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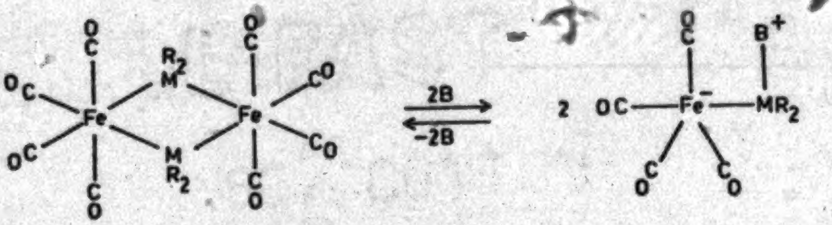
The first two of these compounds have been studied crystallographically, and structures for the other complexes were postulated using mass and infrared spectral and analytical results.[96] However, details of the synthetic routes to all of these compounds remain unpublished.

The structures of 7, 8, and 9 all involve iron-iron bonds. The structure of 10 is presumed to be analogous to that of $[Me_2SnFe(CO)_4]_2$[16] and $[Et_2GeFe(CO)$[illegible][118]

The infrared spectrum of $Ph_2GeFe_2(CO)_8$ (Table II) is consistent with a C_{2v} structure such as 9, a type of structure now quite common in transition metal chemistry. X-ray diffraction studies have confirmed this type of structure for $(Ph_3P)(CO)PtFe_2(CO)_8$[119,120] and $Me_2AsFeMn(CO)_8$[68] and also for the closely related compound, $O_2SFe_2(CO)_8$.[121,122]

It has been discovered that $[Ph_2GeFe(CO)_4]_2$, **10**, undergoes two interesting types of reaction. Marks and Newman[123] have found that **10**, as well as other organogermanium, -tin, and -lead analogues, undergoes a facile and reversible homolysis of the metal-metal bond by Lewis bases, according to the equilibrium:



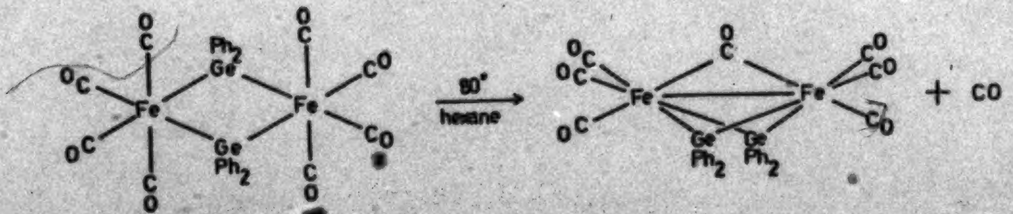
(II-1)

$M = Ge, Sn, Pb;\ R = Me, Ph, t\text{-}C_4H_9;$

B = THF, pyridine, acetone, etc.

In two cases where the base, B, is pyridine, it was possible to isolate the adducts $(MR_2B)Fe(CO)_4$ in the solid state ($MR_2 = GeMe_2$, $Sn(t\text{-}C_4H_9)_2$).

The compound, $[Ph_2GeFe(CO)_4]_2$, also undergoes thermal loss of one molecule of CO to form $(Ph_2Ge)_2Fe_2(CO)_7$[44]:

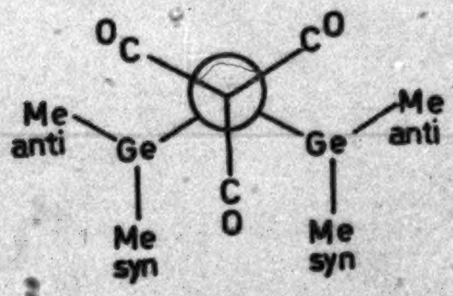


(II-2)

10 **7**

As will be seen in the results and discussion, the loss of carbon monoxide to form 7 also occurs photochemically. The fact that the molecular ion of 10 was not observed in the mass spectrum, with instead the ion of highest mass being that due to 7, is readily understandable in view of this conversion.

Also of special interest, $(Ph_2Ge)_2Fe_2(CO)_7$ possesses a close structural relationship with a number of other complexes which exhibit inequivalent groups on the bridging atom. In nmr spectra, $[F_2PFe(CO)_3]_2$[124] and $[Me_2SFe(CO)_3]_2$[125] show two types of fluorine atoms or methyl groups, respectively. Adams and Cotton[126] have studied the non-rigid behavior of $[Me_2GeCo(CO)_3]_2$ in solution. The nmr spectrum of this compound shows one methyl resonance at room temperature, splitting to two signals at -70°, corresponding to the *syn* and *anti* methyl groups, shown in the Newman projection, 11:



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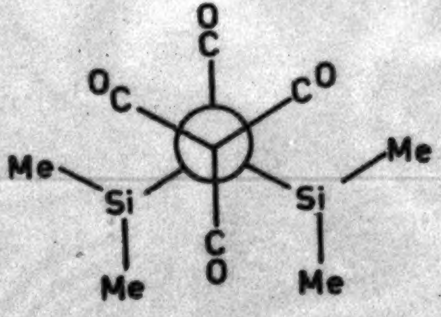


12

The same type of fluxional behavior was found for $(Me_2Si)_2Fe_2(CO)_7$,[127] 12, and would be expected for

$(Me_2Ge)_2Fe_2(CO)_7$, although the nmr spectrum was not reported in the original work.[96] For $(Ph_2Ge)_2Fe_2(CO)_7$, the broadness of the phenyl resonances would probably obscure the existence of two absorptions for the *syn* and *anti* groups.

The study of the reactions of organogermanes, in particular of Ph_2GeH_2, with $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, was undertaken firstly to further the knowledge of the types of reactions and reaction products to be expected from these compounds, and secondly to elucidate some inconsistencies (*vide infra*) in the products of the thermal reaction of $Fe_3(CO)_{12}$ with Ph_2GeH_2.

RESULTS AND DISCUSSION

A. The Reaction Between Ph_2GeH_2 and $Fe(CO)_5$

The photochemical reaction of Ph_2GeH_2 and $Fe(CO)_5$ in mole ratios varying from 1:1 to 3:1, over a period of approximately 40 hours in hydrocarbon solvents, yielded five compounds containing iron-germanium bonds: $(Ph_2Ge)_2Fe_2(CO)_7$, **7**, $Ph_2GeFe_2(CO)_8$, **9**, $(Ph_2Ge)_3Fe_2(CO)_6$, **13**, $(PhGe)_2Fe_3(CO)_9$, **14**, and $[(Ph_2Ge)_2O]Fe_2(CO)_8$, **15**. The structure of **13** would be analogous to that of **8** and $(RGeH)(R_2Ge)_2Fe_2(CO)_6$ (R = Me, Ph).[17,44] A discussion of the structures of **14** and **15** will be given later. All of the above compounds are unstable in solution at room temperature under nitrogen. Complete decomposition occurs within 48 hours for all except **15**, which takes much longer. Because of the long reaction times, during which much decomposition takes place, the yields of most of the products are very low; **15**, the most abundant product, is always formed in less than ten percent yield.

A reasonable first step in the formation of these products would be the photochemically induced loss of carbon monoxide from iron pentacarbonyl:

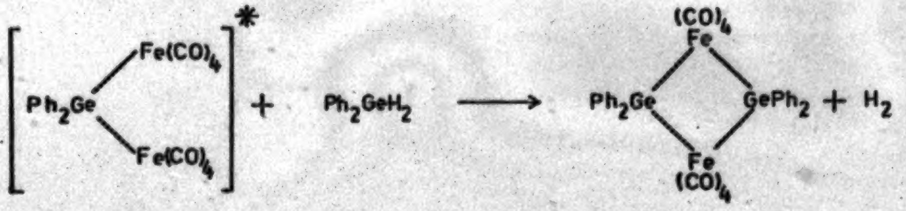
$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4^* + CO \tag{II-3}$$

Infrared spectral evidence exists for the formation of the electronically unsaturated $Fe(CO)_4^*$ from $Fe(CO)_5$

in solid matrices at 4° and 20° K.[128] Although the schemes proposed for the succeeding reactions are based solely on the structures of the products formed, $Fe(CO)_4^*$ could be expected to react with molecules of Ph_2GeH_2 and $Fe(CO)_5$, concurrently or successively, with elimination of H_2 and CO to produce 9:

$$Fe(CO)_4^* + Ph_2GeH_2 + Fe(CO)_5 \rightarrow \underset{9}{Ph_2GeFe_2(CO)_8} + H_2 + CO \qquad \text{(II-4)}$$

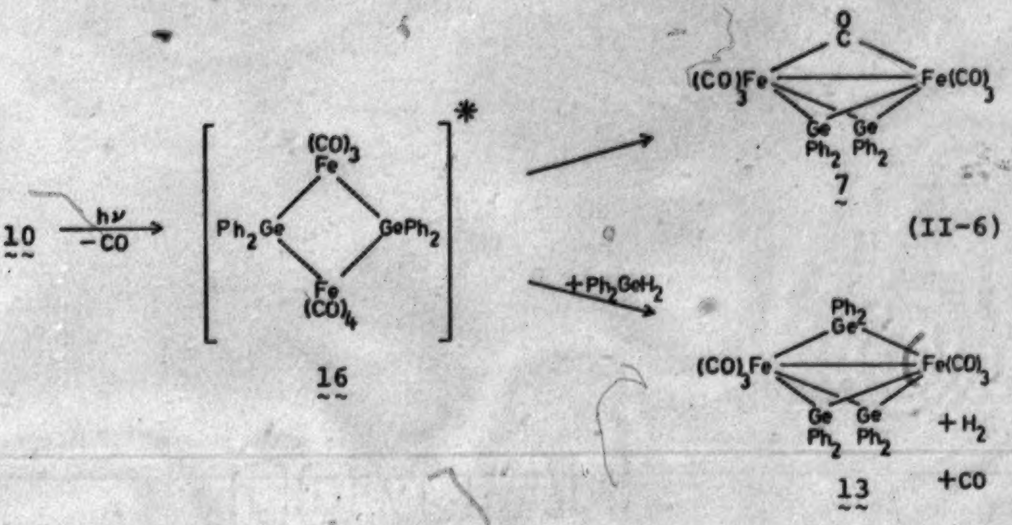
At some time before the iron-iron bond in 9 is formed, 10 may be formed by reaction with another molecule of Ph_2GeH_2. Alternatively, 9 may be photochemically activated to allow insertion of Ph_2GeH_2 with loss of hydrogen:



(II-5)

10

The photochemically-induced loss of CO from 10 would lead to either 7, in the absence of more germane, or 13, on the addition of Ph_2GeH_2 to the unsaturated species 16:



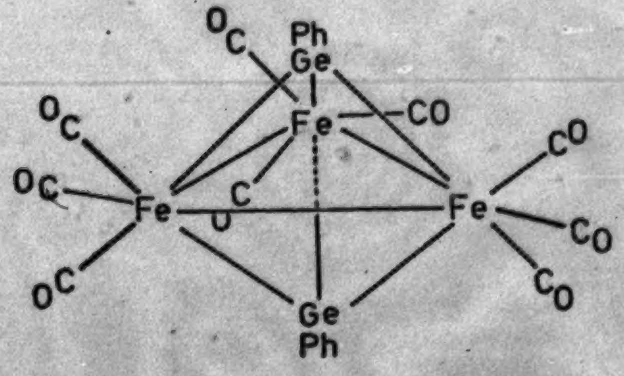
(II-6)

(II-7)

Compound 15 follows directly from 7 by decomposition (*vide infra*).

$7 \rightarrow [(Ph_2Ge)_2O]Fe_2(CO)_8$, 15 (II-8)

The formation of 14 could possibly arise from loss of a phenyl group from 10, subsequent attack by $Fe(CO)_5$ on the unsaturated germanium atom, formation of iron-



14

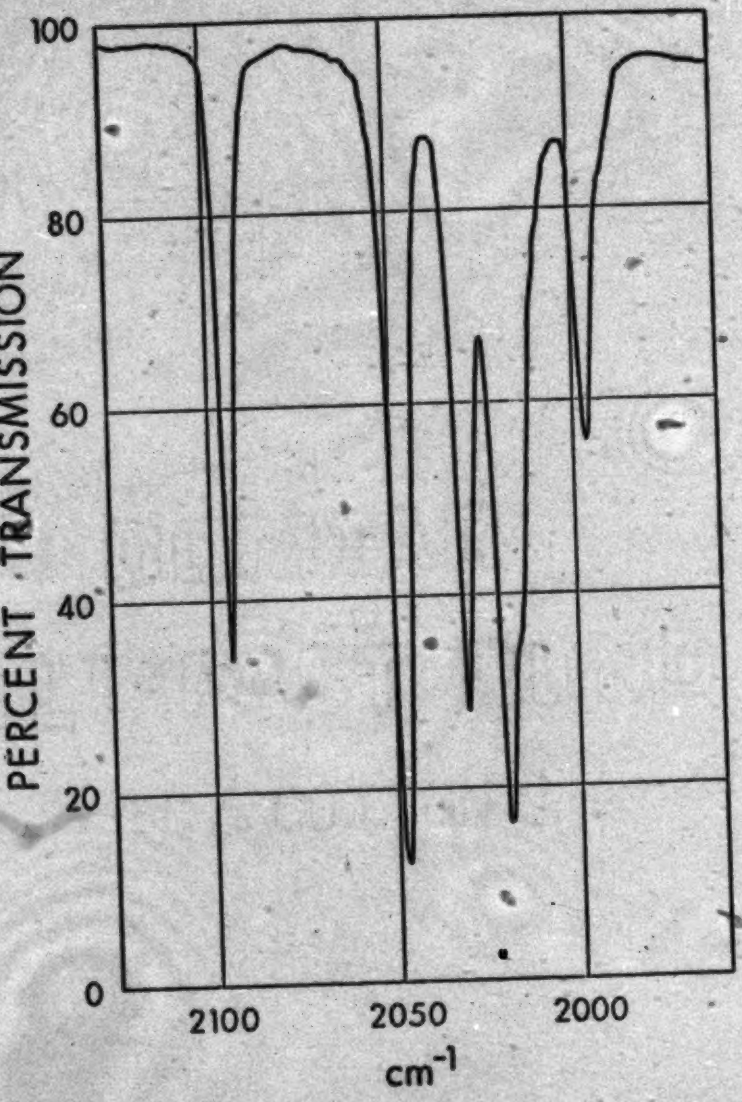
iron bonds with loss of CO, and finally loss of a phenyl group from the second diphenylgermyl group. It is unlikely that 14 is formed from an initial $PhGeH_3$ impurity, since use of $PhGeH_3$ in a similar reaction gave no trace of 14 (*vide infra*).

Although the reaction scheme presented is highly speculative, the reaction intermediates are based on the most rational and direct routes to the formation of the iron-germanium groupings from the available species. The formation of 14 requires the greatest degree of rearrangement of reactive intermediates as well as the breaking of relatively strong germanium-carbon bonds, and is thus most open to question. The formations of the products in reactions II-6 and II-8, which do not require addition of Ph_2GeH_2 to a reactive species, have been confirmed by further studies.

The next sections, B and C, will deal with the characterization of 15 and its preparation from 7. Section D will deal with the conversion of 10 to 7, and section E will discuss the structures and spectra of 13 and 14.

B. The Characterization of $[(Ph_2Ge)_2O]Fe_2(CO)_8$, 15

The solution infrared spectrum of $[(Ph_2Ge)_2O]Fe_2(CO)_8$ in the carbonyl stretching region (Fig, 1, Table II) shows six bands, indicative of a fairly unsymmetrical



$[(Ph_2Ge)_2O]Fe_2(CO)_8$

Figure 1

structure. This is not inconsistent with its now known C_2 molecular symmetry, for which group theory would predict eight bands (4A + 4B). The absence of the extra two bands may be due to accidental degeneracy or to naturally weak vibrational intensity.

The infrared spectrum of 15 as a KBr disc (Table III), exhibits a medium strength band at 794 cm^{-1}, which can be assigned to the germanium-oxygen stretching frequency. Usually Ge-O-Ge groupings show a range of stretching frequencies of 800 to 900 cm^{-1},[129] although the frequency has been recorded as low as 680 cm^{-1} and as high as 1040 cm^{-1},[130] for alkyldigermoxanes. The absorption for $(Ph_3Ge)_2O$ in the solid state occurs at 858 cm^{-1}.[130] The nearest absorption bands in the spectrum of 15 to the assigned digermoxane stretching frequency are two bands at 693 and 729 cm^{-1}, both of which are characteristic of carbon-hydrogen bending motions in monosubstituted benzene rings.[131] The diagnostic absorptions for phenylgermanium groups[129] are prominent at 1077 and 1427 cm^{-1}.

The mass spectrum of an analytically pure sample of 15 run at a source temperature of 130°, exhibits peaks due to the molecular ion of 15, as well as those of 7 and 9, although all molecular ions are weak (see Table IV, Fig. 2). Obviously there must be facile rearrangement to form these other compounds, either during thermal decomposition or after molecular ionization. At source temperatures lower than 130°, no ions are seen; on increasing the source temperature to 145°, peaks due to 15 fall off rapidly, and those due to 7 and 9 increase drastically. At 130°, the consecutive loss of carbon

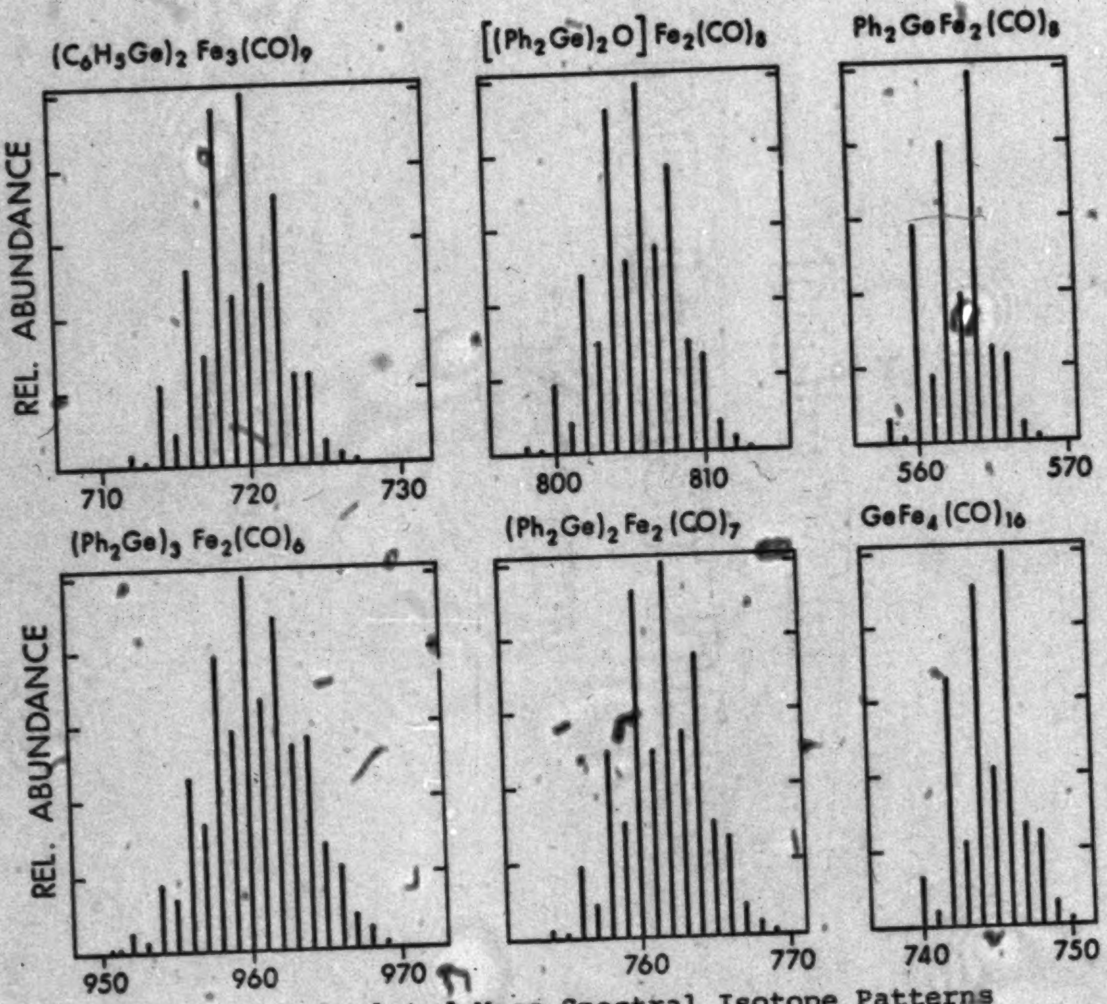


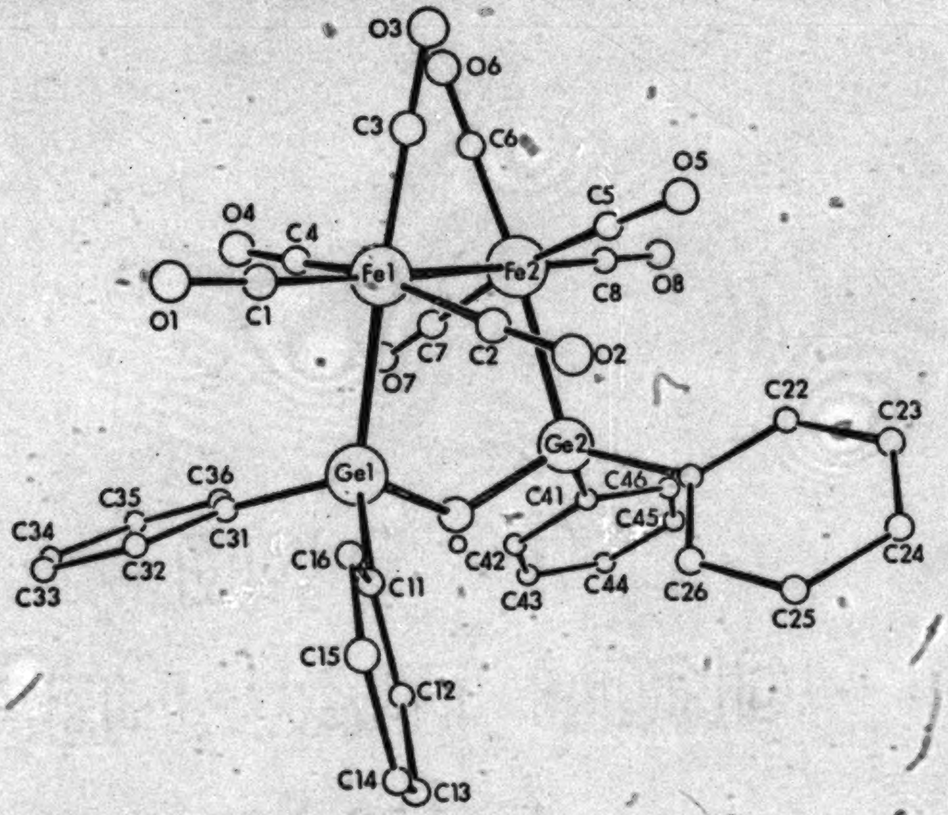
Figure 2 Calculated Mass Spectral Isotope Patterns

(Observed patterns closely coincided with calculated patterns in all cases.)

monoxide ligands from all three parent ions is apparent in the spectrum. Also evident are rearrangement or recombination peaks assigned to Ph_4GeFeO^+ and Ph_3Ge^+. In contrast, the mass spectra of pure samples of 7 and 9 show only the expected fragmentation patterns from the molecular ions, and the ubiquitous Ph_3Ge^+.

The formulation, structure, and even purity of 15 were initially in doubt because of the existence of these extra peaks in the mass spectrum, and also because the analytical data for two of these compounds are very similar; *viz.*, for 7 and 15, calculated percentages for carbon are, respectively, 47.7 and 48.9, and for hydrogen, 2.28 and 2.65. The molecular weight of 15 is 805, and that of 7 is 761, while the osmometric determination for 15 in CH_2Br_2 was 788. The identity of 15 was not known until a single crystal X-ray structural determination was carried out by Dr. A. S. Foust in this department. The molecular structure is shown in Figure 3, along with selected bond lengths and angles.[132]

Each iron atom is approximately octahedrally coordinated to four carbonyl ligands, one germanium atom, and one iron atom. The two iron atoms join in such a way that the equatorial ligands on each iron (perpendicular to the iron-iron bond) are staggered with respect to the equatorial ligands on the other iron. Therefore this structure may be figuratively derived from the nonbridged D_{4d} structure of $Mn_2(CO)_{10}$,[20] 5, by the replace-



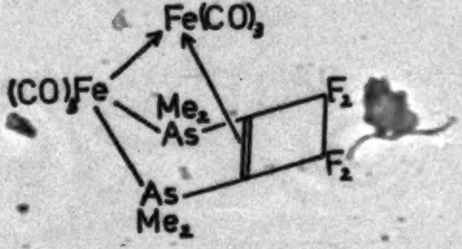
Molecular Structure of $[(Ph_2Ge)_2O]Fe_2(CO)_8$

Bond Lengths (Å)		Bond Angles (°)	
Fe(1)-Fe(2)	2.881(3)	Ge(1)-Fe(1)-Fe(2)	92.7(1)
Fe(1)-Ge(1)	2.462(3)	Ge(2)-Fe(2)-Fe(1)	89.5(1)
Fe(2)-Ge(2)	2.474(3)	Fe(1)-Ge(1)-O	109.9(3)
Ge(1)-O	1.780(8)	Fe(2)-Ge(2)-O	107.6(3)
Ge(2)-O	1.788(8)	Ge(1)-O-Ge(2)	125.6(5)

Figure 3

ment of an equatorial carbonyl ligand on each transition metal with the bidentate ligand $Ph_2GeOGePh_2$. The three-atom bridging unit ($Ph_2GeOGePh_2$) seems flexible enough to allow the carbonyl ligands to adopt the staggered configuration characteristic of dimers supported by a lone σ bond.

The long iron-iron bond distance of 2.881(3) Å is characteristic of a non-bridged bond, and is even longer than the distance of 2.787(2) Å, reported for the unbridged $Fe_2(CO)_8^{=}$ anion.[133] The unconstrained iron-iron distance in $Fe_2(CO)_6Me_4As_2C_4F_4$, 17, is 2.88 Å.[134]



17

Although iron-iron bond lengths exhibit large variations, most bridged complexes have shorter iron-iron bond lengths, e.g. 2.558-2.683 Å in $Fe_3(CO)_{12}$.[135] The compound, $C_6F_4Fe_2(CO)_8$, which has eclipsed carbonyl ligands and a bridge made up of two carbon atoms, has an iron-iron distance of 2.797(1) Å.[136] The longest iron-iron bond seems to be 3.05 Å in $[Fe(NO)_2I]_2$,[137] which has two bridging iodine atoms. Other reported iron-iron bond lengths for octacarbonyl complexes are 2.758(8) Å in $(Ph_3P)(CO)PtFe_2(CO)_8$,[120] 2.717(4) Å in $Fe_2(CO)_8SO_2$,[122] 2.87(1) Å in $SnFe_4(CO)_{16}$,[138] and 2.635(3) Å in $Ph_2CCFe_2(CO)_8$.[139] The last four compounds all have single atom bridges between the iron atoms.

The iron-germanium bond lengths of 2.462(3) and 2.474(3) Å in **15** seem to be the second longest such bonds known. Other iron-germanium bond lengths for a germanium atom unconstrained by an iron-iron bond are 2.357(4) Å in $Cl_2Ge[Fe(CO)_2Cp]$,[140] 2.377(2) and 2.367(3) Å in $[CpFe(CO)_2GeMe_2]_2O$,[117] 2.433(8) Å in $[CpCo(CO)]_2(GeCl_2)_2$-$Fe(CO)_4$,[104] 2.342(2) Å in η-$C_3H_5Fe(CO)_3GeCl_3$,[18] 2.28 and 2.29 Å in $Cp(C_4H_6)FeGeCl_2Me$ (two crystal modifications),[116] and 2.492 Å in $[Et_2GeFe(CO)_4]_2$.[118]

Three iron-germanium bond lengths across an iron-iron bond are 2.346(1) Å (average) in $Cp_2Fe_2(CO)_3GeMe_2$,[141] 2.398(5) Å in $(Me_2Ge)_3Fe_2(CO)_6$,[17] and 2.425(3) Å in $(Ph_2Ge)_2Fe_2(CO)_7$.[98] The extreme shortness of the bond in $Cp(C_4H_6)FeGeCl_2Me$ was attributed to "a strong dπ(Fe)→dπ(Ge) back-donation, which is favoured both by the relatively weak π-acceptor ability of the iron atom ligands (C_5H_5 and C_4H_6) and by the electronegative substituents, chlorine atoms, at the germanium atom."[116] Using the opposite argument, the long iron-germanium bonds in **15** and $[Et_2GeFe(CO)_4]_2$ would be due to the strong π-acceptor ability of the carbonyl ligands, which decreases the amount of dπ(Fe)→dπ(Ge) back-donation. The long bonds, however, are still somewhat shorter than 2.56 Å, the sum of the single-bonded covalent radii for iron (1.34 Å)[19] and germanium (1.22 Å).[142] This indicates at least some degree of π-bonding between iron and germanium.

C. The Conversion of $(Ph_2Ge)_2Fe_2(CO)_7$, 7, to $[(Ph_2Ge)_2O]Fe_2(CO)_8$, 15

A feature of 7 which had not been satisfactorily explained[143] in the original synthesis[134] is the fact that a hydrocarbon solution showed more terminal carbonyl absorptions (7) than would be expected for this type of molecule of C_{2v} symmetry (5). The molecular structure, elucidated by an X-ray crystal study by Dr. M. Elder,[98] is shown in Figure 4, along with selected bond lengths and bond angles. This molecule is formally obtained by replacing two bridging carbonyl ligands in $Fe_2(CO)_9$[144] by two Ph_2Ge groups. Group theory would predict $2A_1 + 2B_1 + 1B_2$ terminal carbonyl stretching bands, as well as one bridging carbonyl band. It has now been found that two of the seven terminal carbonyl absorptions seen in the original infrared spectrum are due to a decomposition product which forms slowly at room temperature in solution. If a crystalline sample of 7 is dissolved in hexane* at 0°, and the infrared

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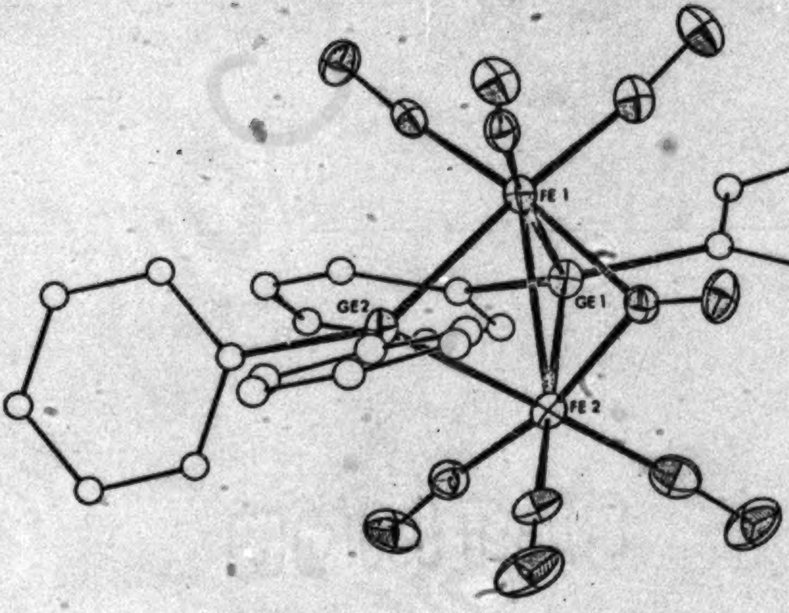
*Hereafter heptane and hexane refer to *n*-heptane and *n*-hexane.

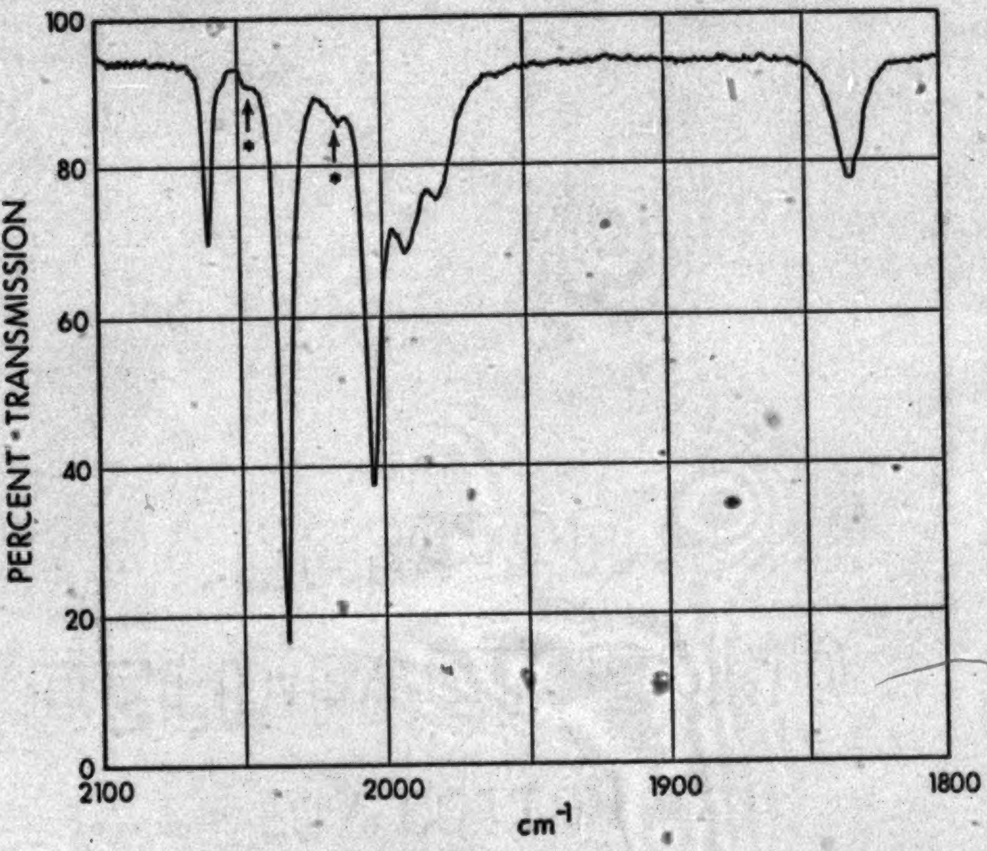


Molecular Structure of $(Ph_2Ge)_2Fe_2(CO)_7$

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-Fe(1)	2.416(3)	Fe(1)-Ge(1)-Fe(2)	66.7(1)
Ge(1)-Fe(2)	2.432(3)	Fe(1)-Ge(2)-Fe(2)	66.8(1)
Ge(2)-Fe(1)	2.402(3)		
Ge(2)-Fe(2)	2.440(3)		
Fe(1)-Fe(2)	2.666(3)		

Figure 4

spectrum is run immediately, one obtains the six band spectrum shown in Figure 5. On warming to room temperature the new bands of the decomposition product increase in intensity, and the bands of 7 disappear slowly, as shown in Figure 6. After about 16 hours, along with an insoluble decomposition product, the yellow solution shows only bands due to 15, $[(Ph_2Ge)_2O]Fe_2(CO)_8$ (Fig. 1).

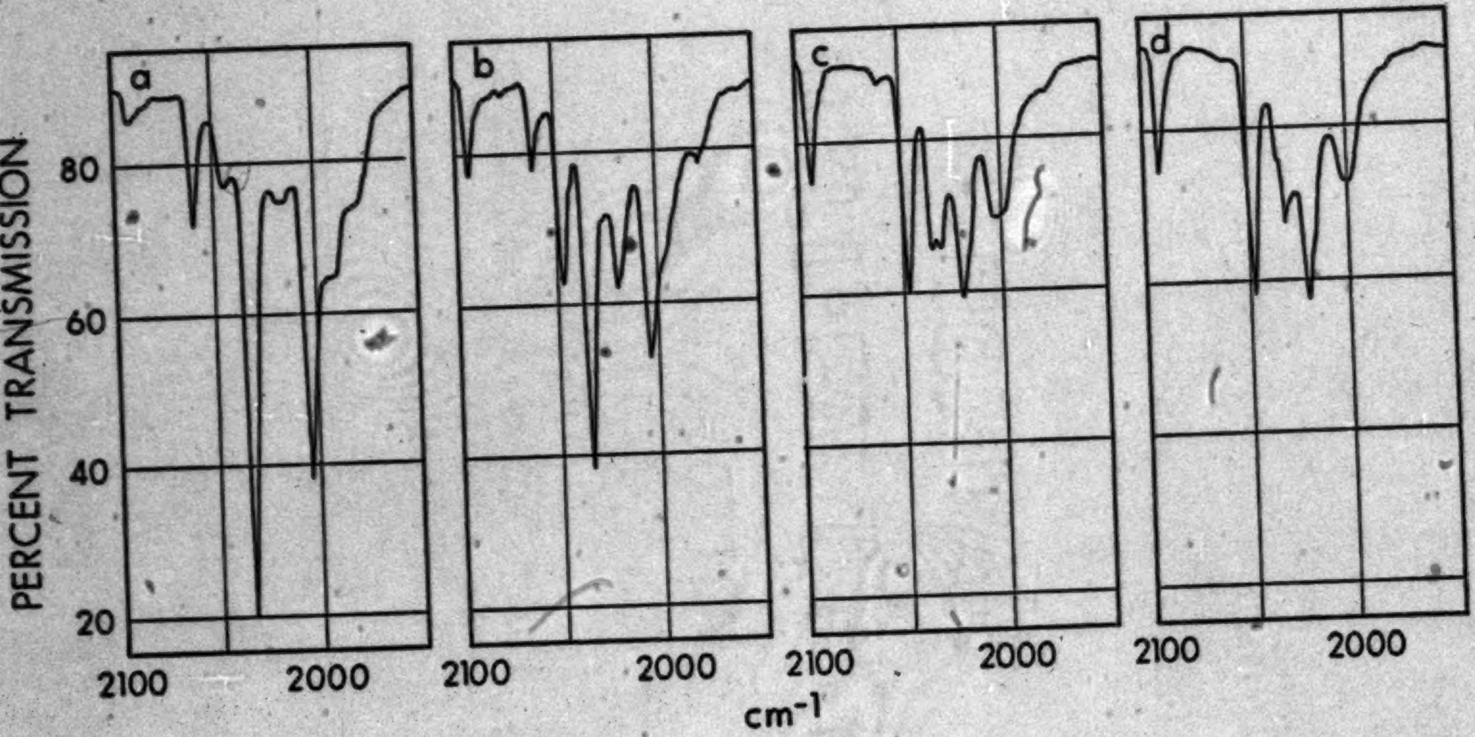


$(Ph_2Ge)_2Fe_2(CO)_7$

*Due to formation of $[(Ph_2Ge)_2O]Fe_2(CO)_8$

Figure 5

Clearly this reaction must involve considerable decomposition of 7 to other products, since 15 contains one extra carbonyl ligand and one extra oxygen atom. Since the hydrocarbon solvent was previously distilled from sodium wire, under dry nitrogen, the solvent would be free of dissolved water and oxygen. The only other possible source of the oxygen atom in the digermoxane linkage would be a carbonyl ligand in the starting material.



Decomposition of $(Ph_2Ge)_2Fe_2(CO)_7$

a After 15 min. c After 5 hours

b After 1 hour d After 9 hours

Figure 6

In a further experiment to try to establish conclusively the source of the extra oxygen atom, five solutions of **7** were allowed to decompose to **15** in Schlenk tubes under different conditions. The samples were obtained from a stock solution of **7**, suitable for direct infrared sampling (c. 1.3 x 10^{-3} M), and made up at 0° with heptane freshly distilled from sodium wire. Of the five solutions, one each under an atmosphere of CO, O_2, 1:1 mixture of CO and O_2, N_2, and helium with a small amount of water added to the mixture, the solution under N_2 decomposed slowest, followed by the solutions under CO, He, CO + O_2, and O_2, in that order. The solution under CO eventually gave by far the largest amount of **15**, as shown by comparing the intensities of the infrared bands in spectra of the five solutions. It is not surprising that the solutions under O_2 decomposed giving very little of **15**, since a solution of **7**, after being exposed to air for 24 hours, shows no absorptions in the CO region of the infrared spectrum. The solutions under helium and pure CO decomposed at about the same rate, but far less of **15** formed under helium. Although there was much decomposition to insoluble products in all five cases, the evidence indicates that most probably the oxygen atom in the digermoxane linkage originates from a carbonyl ligand on **7**. Whether the germanium-oxygen bonds are formed while the oxygen atom is bound to a carbon atom in free or complexed carbon monoxide is still unknown, as is the fate of the extra carbonyl carbon atom.

The decomposition is certainly thermally controlled, for the reaction also took place in the absence of light at room temperature. However, the reaction took much longer to go to completion in the dark. Therefore it would seem that fluorescent light also plays a part in the reaction.

There are a number of precedents for the incorporation of oxygen atoms into transition metal complexes or decomposition products from sources other than molecular oxygen or recognized oxidizing agents. These reactions mainly involve the formation of silicon-oxygen bonds.

Kaska and coworkers[145] have found that a facile carbon monoxide cleavage occurs in the reaction of hexaphenylcarbodiphosphorane with manganese pentacarbonyl bromide in benzene at 40°:

$$Mn(CO)_5Br \; + \; Ph_3P{=}C{=}PPh_3 \; \rightarrow \; Br(CO)_4Mn{=}C{=}C{=}PPh_3 \; + \; Ph_3P{=}O \qquad (II\text{-}9)$$

The phosphine oxide and manganese complex were formed in equimolar quantities, with both products being identified by infrared and mass spectra, and the transition metal complex by an X-ray crystal structure.[146]

The reaction of $Fe(CO)_4PMe_2Cl$ with $NaM(CO)_5$ (M = Mn or Re) was reported by Ehrl and Vahrenkamp[147] to give as one of the products the unexpected $[(CO)_4FePMe_2]_2O$. The authors think it unlikely that the oxygen atom in the diphosphorane bridge comes from a carbonyl ligand because there is little decomposition. The probable source is the solvent, THF, since nmr spectra indicated that long-chained alkanes were formed in the conversion.

In spite of the presence of the solvent THF, Curtis[148,149] attributes the formation of hexaphenyldisiloxane, in reactions of triphenylchlorosilane with numerous transition metal carbonyl anions, to oxygen from the carbonyl groups. In every case when the expected neutral triphenylsilyl metal complex is not obtained, $(Ph_3Si)_2O$ is formed, while, when the expected product is isolated, there is no evidence for a disiloxane. Curtis cites as evidence work by Shrieke and West,[150] where $(Ph_3Si)_2O$ is formed in the reaction of $Ph_3SiMn(CO)_5$ with PPh_3 in benzene under anhydrous and oxygen-free conditions. Other researchers have found that solid $Me_3SiCo(CO)_4$,[151] liquid $H_3SiCo(CO)_4$,[152] and $CpM(CO)_3SiMe_3$ (M = Mo, W) in solution[153] decompose to $(Me_3Si)_2O$ or $(H_3Si)_2O$, among other products, at room temperature. However, when $Me_3SiCo(CO)_4$ is heated at 105° for 50 hours, migration of the trimethylsilyl group from cobalt to oxygen takes place to give two compounds, reported to be $Me_3SiOCCo_3(CO)_9$ and $(Me_3SiOC)_4Co_2(CO)_4$.[154] *

*When the decomposition reaction was carried out in this laboratory by Dr. A. C. Sarapu, no trace of $Me_3SiOCCo_3(CO)_9$ was found, and the other compound more probably is $(Me_3SiOC)_4Co_2(CO)_5$, whose structure could be analogous to that of $(Me_3SiOC)_4Fe_2(CO)_6$.[155]

Electrophilic attack at carbonyl oxygen was also used to rationalize the formation of compounds such as $MeCl_2SiOCCo_3(CO)_9$ from $Co(CO)_4^-$ and $MeSiCl_3$.[156]

Another reaction involving attack of a trimethylsilyl group at a carbonyl oxygen is evidenced by the formation and X-ray structural characterization of $(Me_3SiOC)_4Fe_2(CO)_6$.[155] It was not determined whether the reaction of Me_3SiBr with $Na_2Fe(CO)_4$ to give $(Me_3SiOC)_4Fe_2(CO)_6$ involves initial formation of an iron-silicon bond, with subsequent silicon migration, or whether a silicon-oxygen bond is formed directly.

A very recent paper by Cotton and coworkers[117] reports the formation of $[CpFe(CO)_2GeMe_2]_2O$ by the air oxidation of $(CpFeCO)_2(CO)GeMe_2$. This is the second incidence of the formation of a digermoxane bridging group, in this case between two non-bonded iron atoms. However, decomposition of $(CpFeCO)_2(CO)GeMe_2$ does not apparently occur in the absence of air.

The conversion of $(Ph_2Ge)_2Fe_2(CO)_7$ to $[(Ph_2Ge)_2O]$-$Fe_2(CO)_8$ is unique in that the digermoxane linkage forms from a carbonyl oxygen atom. Previous reports involving silicon-oxygen bonds indicated either an uncoordinated disiloxane, or only a monosiloxyl moiety derived from a carbonyl oxygen atom. Nevertheless, from the evidence at hand, the involvement of a carbonyl oxygen atom in the formation of ether-type linkages is well established.

The formation of 15 must involve breaking of two iron-germanium bonds at some point during the decomposition of 7. No matter whether the oxygen atom is from a bound CO ligand or a free CO molecule in solution, the starting material requires two CO groups originally from 7 to form 15. Extensive decomposition of 7 to insoluble products therefore occurs concurrently as expected.

D. The Conversion of $[Ph_2GeFe(CO)_4]_2$, 10, to $(Ph_2Ge)_2Fe_2(CO)_7$, 7

As mentioned in the introduction, the formation of 7 from 10 occurs thermally, when a solution of 10 is heated in an evacuated sealed tube at 80°. The photochemical conversion to 7 was carried out in a separate experiment, using a solution of $[Ph_2GeFe(CO)_4]_2$ in toluene. An infrared spectrum indicated a conversion of over 50 percent after ultraviolet irradiation over four hours at -78°. This suggests that the formation of 7 in the reaction of Ph_2GeH_2 and $Fe(CO)_5$ under photolytic conditions could occur through the decomposition of $[Ph_2GeFe(CO)_4]_2$. However, 10 was not isolated from this reaction, and no evidence was found for it in infrared spectra of the reaction mixtures during photolysis.

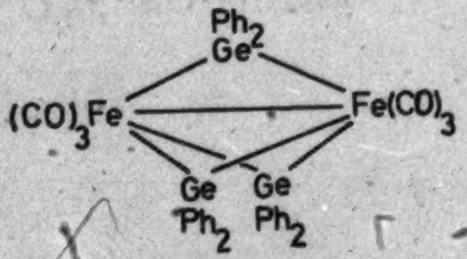
On the other hand, the reverse reaction at 0° and a pressure of 1500 p.s.i. of carbon monoxide showed no trace of 10 after stirring for seven days:

$$(Ph_2Ge)_2Fe_2(CO)_7 \ + \ CO \ \overset{0^{\circ}}{\nrightarrow} \ [Ph_2GeFe(CO)_4]_2 \qquad \text{(II-9)}$$

An infrared spectrum of the solution after seven days showed only **7** and a small amount of $Fe(CO)_5$, and after warming to room temperature, the digermoxane compound, **15**. It is possible that reconversion of **7** to **10** may occur at higher temperatures and pressures, but certainly decomposition to $[(Ph_2Ge)_2O]Fe_2(CO)_8$ would occur concurrently.

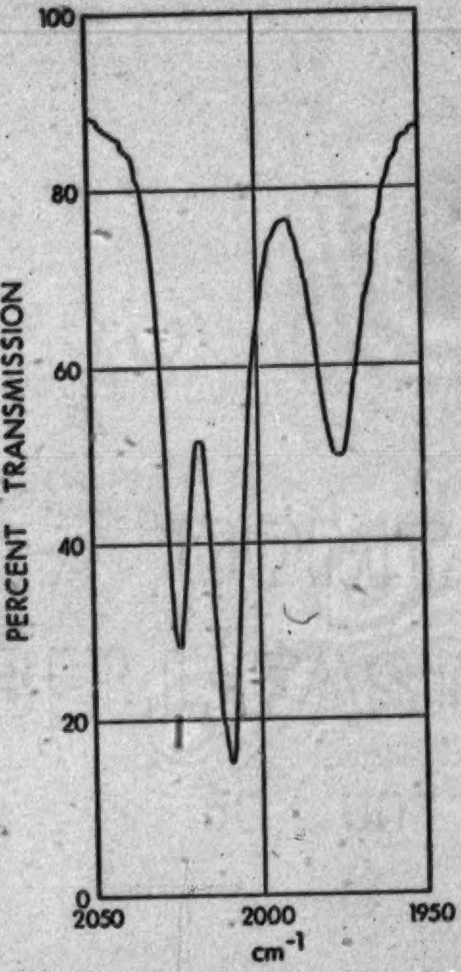
E. The Complexes $(Ph_2Ge)_3Fe_2(CO)_6$ and $(PhGe)_2Fe_3(CO)_9$

The metal cluster compound $(Ph_2Ge)_3Fe_2(CO)_6$, **13**, probably has a structure similar to that for **8**, $(Me_2Ge)_3Fe_2(CO)_6$. The ruthenium and osmium analogues of



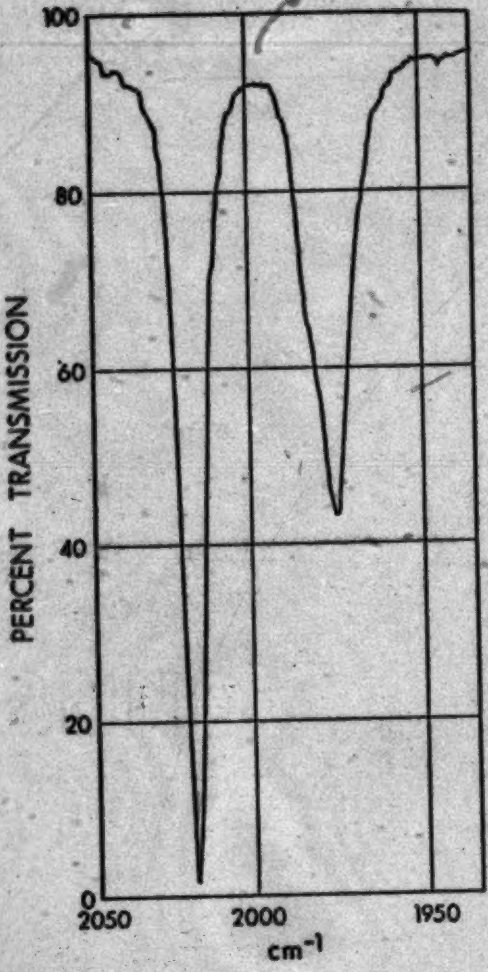
13

8 have also been prepared.[157] The infrared spectrum in the carbonyl region exhibits three bands for **13** (Fig. 7, Table II). The expected D_{3h} symmetry for these compounds should produce a spectrum showing only two bands ($A_2" +$ E'). However, a slight distortion of the molecule would not be unlikely, considering the size of the phenyl groups. The reduction in symmetry from D_{3h} would allow



$(Ph_2Ge)_3Fe_2(CO)_6$

Figure 7



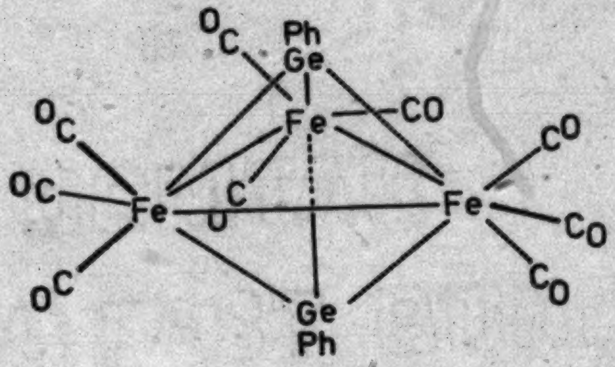
$(PhGe)_2Fe_3(CO)_9$

Figure 8

the appearance of a third carbonyl band. Even for $(Me_2Ge)_3Ru_2(CO)_6$ in cyclohexane, the carbonyl band of lower energy is broad. This suggests that it comprises two near-degenerate absorptions.[157]

The mass spectrum of 13 exhibits the molecular ion at 960 mass units with the expected isotope combination pattern (Fig. 2), as well as the consecutive loss of six carbonyl groups from the parent ion.

The infrared spectrum of $(PhGe)_2Fe_3(CO)_9$, 14, consists of two bands in the carbonyl region, one of which shows a slight dissymmetry on the high energy side (Fig. 8). The most probable molecular structure would be one involving a triangle of iron atoms capped above and below by



14

a phenylgermyl group. Depending on the orientation of the carbonyl ligands around the seven-coordinate iron atoms, the molecule could have a symmetry as high as D_{3h}, but more probably C_{3h}. In both these cases, and in other structures lower in symmetry than C_{3h}, at least three infrared-active carbonyl stretching bands are predicted. The dissymmetry of the low wavenumber band is therefore probably due to a near-degeneracy of two stretching frequencies. A spectrum in a less polar solvent than dichloromethane would be expected to separate or at least make more apparent the overlapping bands, but unfortunately 14 is insoluble in saturated hydrocarbon solvents.

The mass spectrum of **14** exhibits the expected isotope combination pattern for the parent ion (Fig. 2) and the successive loss of nine carbonyl groups.

The compound $As_2Fe_3(CO)_9$, for which the X-ray structural determination shows three iron-iron bonds, exhibits three bands in the carbonyl stretching region in methylcyclohexane solution.[158] The idealized molecular symmetry is C_{3h}, analogous to that shown for **14**.

The closely related compound, $Me_3SiNFe_3(CO)_{10}$,[159] contains triply-bridging CO and Me_3SiN ligands and three iron-iron bonds,[160] of average length 2.535(2) Å. The infrared spectrum in this case, however, exhibits five terminal carbonyl bands and one strong band due to the triply-bridging carbonyl ligand. The larger number of bands undoubtedly arises from the reduction in symmetry through the presence of dissimilar bridging groups. The structure is described by a pseudo-C_3 symmetry with the terminal carbonyl ligands arranged in a way similar to that for $As_2Fe_3(CO)_9$ and **14**.

The phenylgermyl group has previously been proposed as a bridge for a tri-metallic ring system in $PhGeCo_3(CO)_9$,[161] which is presumably analogous to $MeCCo_3(CO)_9$, whose molecular structure has been determined.[162]

F. The Reactions Between Et_2GeH_2 and the Binary Carbonyls of Iron

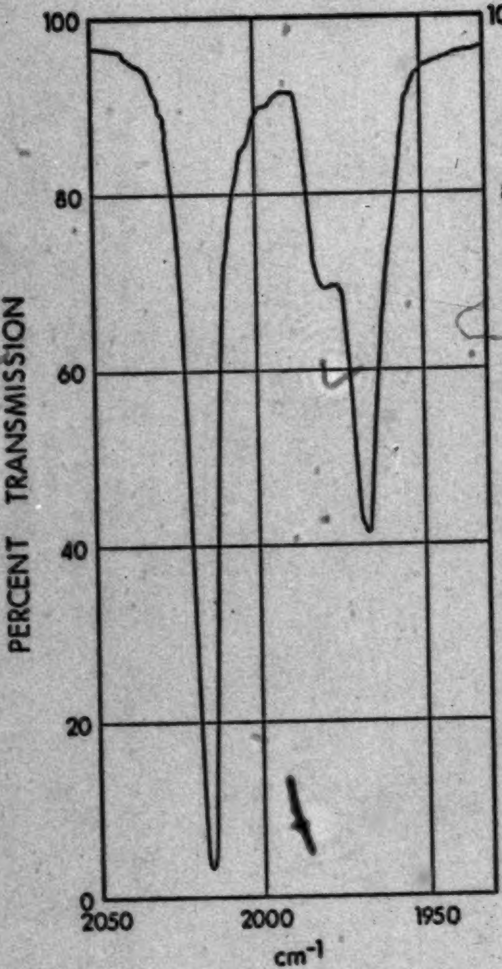
The reactions of Et_2GeH_2 with $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ produced five compounds having analogues derived from Ph_2GeH_2: $(Et_2Ge)_2Fe_2(CO)_7$, 18, $Et_2GeFe_2(CO)_8$, 19, $[Et_2GeFe(CO)_4]_2$, 20, $(Et_2Ge)_3Fe_2(CO)_6$, 21, and $(EtGe)_2Fe_3(CO)_9$, 22. The first three compounds were produced from the thermal reaction with $Fe_2(CO)_9$ and the first four from $Fe_3(CO)_{12}$, while only 20 was not isolated from the photochemical reaction using $Fe(CO)_5$. Thus these reactions parallel those of Ph_2GeH_2 closely, with the triply bridging germanium complexes 14 and 22 forming only photochemically, and the analogues 10 and 20 being isolated only from the thermal reactions.

Whereas 10 did not show the molecular ion in the mass spectrum, but instead a spectrum identical to that of 7, 20 shows the molecular ion and the consecutive loss of eight carbonyl ligands. Nevertheless, when a heptane solution of 20 was heated in an evacuated sealed tube at 80° for 20 hours, there was about 30 percent conversion to 18, as estimated from an infrared spectrum. This parallels the conversion of 10 to 7. However, 18 does not decompose in solution at room temperature under nitrogen, unlike its diphenyl analogue, 7, which gives the digermoxane complex, 15.

As can be seen from Table II, the infrared spectra of most pairs of analogous phenyl and ethyl derivatives are similar, with the bands of the ethyl derivatives usually several wavenumbers lower than those of the corresponding phenyl derivatives. Although the shifts are not great, the consistent variation probably reflects a greater σ-donation from and/or smaller π-back donation to the EtGe- and Et_2Ge- groups. The three band carbonyl spectrum of 22 (Fig. 9) is a verification of the proposed third band in the spectrum of $(PhGe)_2Fe_3(CO)_9$ (Fig. 8).

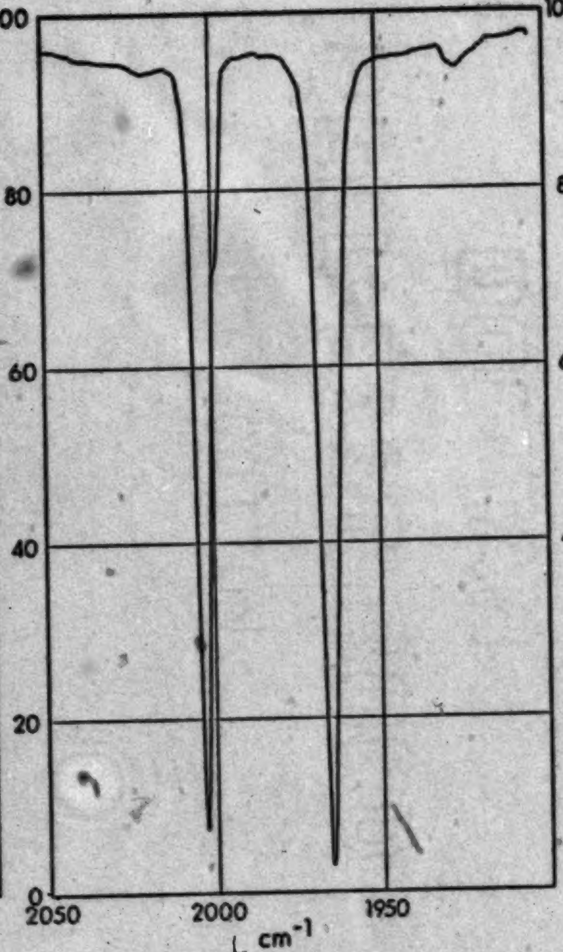
Compound 21 exhibits a band pattern somewhat different from its analogous phenyl derivative, 13. In heptane solution there are two very strong carbonyl bands (Fig. 10). The band at 1965 cm^{-1} is slightly stronger than that at 2003 cm^{-1}. In dichloromethane, however, the intensity pattern changes, so that the high energy band at 2000 cm^{-1} is much more intense than that at 1960 cm^{-1}, which has also broadened considerably (Fig. 11). This decrease in absorption intensity, coupled with band broadening, is consistent with a nearer degeneracy of a two-mode absorption at the low energy band in heptane than in dichloromethane. The appearance of a third band has been inferred before in the case of $(Me_2Ge)_3Ru_2(CO)_6$,[157] where the phenomenon of relative intensity changes was also employed.

The compounds 18, 19, and 22 were sufficiently unstable in solution or produced in such small yields



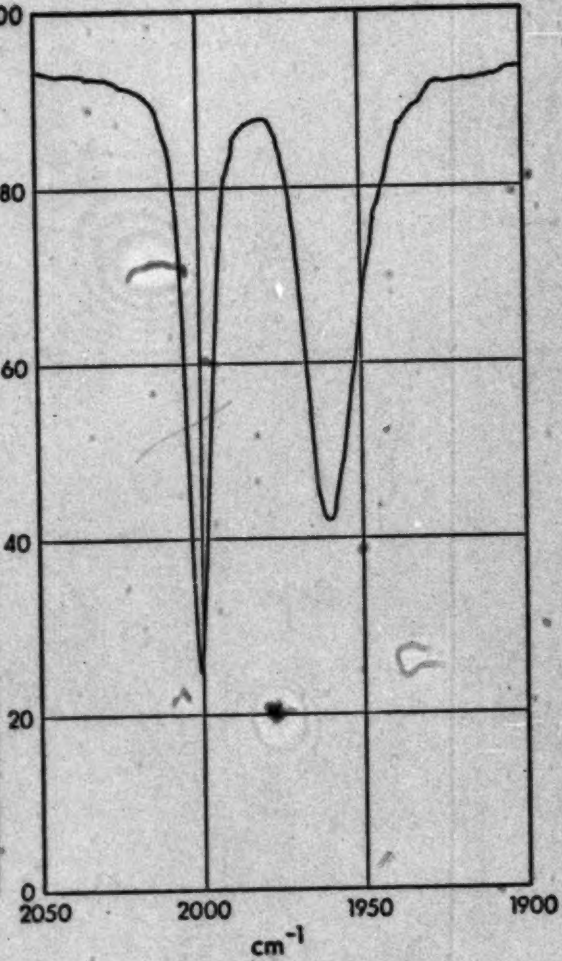
$(EtGe)_2Fe_3(CO)_9$

Figure 9



$(Et_2Ge)_3Fe_2(CO)_6$ in heptane

Figure 10



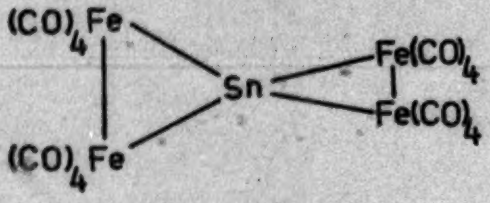
$(Et_2Ge)_3Fe_2(CO)_6$ in dichloromethane

Figure 11

that crystalline materials suitable for analysis were never obtained. Fractional sublimation, often a successful method of purification for analytical samples, was not useful in this case, because all three compounds sublimed within similar ranges of temperature and pressure, accompanied by thermal decomposition. The formulation of these compounds is not in doubt, however, since mass spectra exhibited molecular ions and expected fragmentation patterns and infrared spectra were reasonably similar to those of the analogous phenyl compounds.

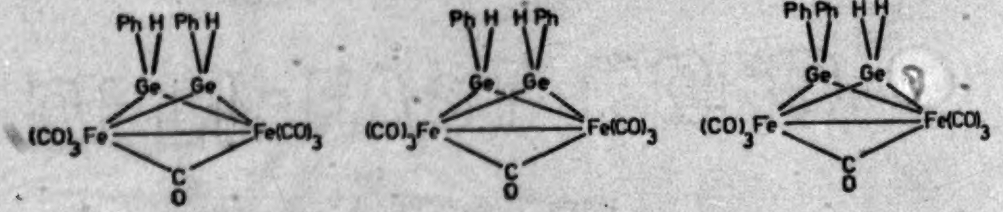
G. Reactions Between $PhGeH_3$ and the Binary Carbonyls of Iron

In an attempt to synthesize $(PhGe)_2Fe_3(CO)_9$ in greater yield, $PhGeH_3$ was reacted with $Fe(CO)_5$ in heptane under the same photochemical conditions as with Ph_2GeH_2. The only identifiable product obtained was $GeFe_4(CO)_{16}$, whose infrared spectrum, but not synthesis, has already been reported.[94,95] The expected isotope pattern for the molecular ion as well as the consecutive loss of 16 CO groups was exhibited by the mass spectrum. An X-ray structural study on the tin analogue, $SnFe_4(CO)_{16}$, **23**, has already been carried out.[138] The molecule contains a tetrahedrally coordinated central tin atom, bonded to two sets of $Fe_2(CO)_8$ groups each containing one iron-iron bond.



23

From the sealed tube thermal reactions of $PhGeH_3$ with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, two products were obtained. The major product, the analogue of 7, was $(PhGeH)_2Fe_2(CO)_7$, 24, whose infrared (Table II) and mass spectra would not differentiate the three possible isomers:



24

The mass spectrum exhibited a molecular ion and consecutive loss of seven carbonyl ligands and two hydrogen atoms to give a peak at 412 mass units corresponding to $(PhGeFe)_2^+$. Unfortunately, the thermal instability of 24 in solution did not allow isolation of a sample pure enough for an nmr spectrum or a microanalysis. However, the evidence from the mass spectrum and the similarity of its infrared spectrum with the analogues 7 and 18 are sufficient to establish the composition of the complex.

The second compound isolated from these reactions proved to be $GeFe_4(CO)_{16}$. At no point during the workup of these reaction mixtures was there any evidence, either infrared or mass spectral, for the formation of the desired compound, $(PhGe)_2Fe_3(CO)_9$.

H. The Reactions Between Ph_3GeH and $Fe(CO)_5$ and $Fe_3(CO)_{12}$

The reaction of Ph_3GeH and $Fe(CO)_5$ under ultraviolet light produced as the only identifiable products, $(Ph_2Ge)_2Fe_2(CO)_7$, **7**, and $[(Ph_2Ge)_2O]Fe_2(CO)_8$, **15**. The oxidative elimination product to be expected from this reaction, $Ph_3GeFe(CO)_4H$, has been shown[47] to be unstable under the conditions used in this work. The synthesis of $Ph_3GeFe(CO)_4H$ is effected at 0° by the protonation of $[Ph_3GeFe(CO)_4]^-$ using HCl in THF solution. In solution under nitrogen, $Ph_3GeFe(CO)_4H$ decomposes to insoluble products on warming to room temperature.

In contrast to the photochemical reaction with $Fe(CO)_5$, Ph_3GeH and $Fe_3(CO)_{12}$ in a sealed tube heated at 80° produced only one compound containing germanium. The complex $Ph_2GeFe_2(CO)_8$, **9**, isolated after chromatography on Florisil, was characterized by its infrared spectrum, isotope combination pattern (Fig. 2), and exact mass of the parent ion in the mass spectrum.

The synthesis of $Ph_2GeFe_2(CO)_8$ can also be effected by the displacement of chloride ions in Ph_2GeCl_2 with $Fe_2(CO)_8^{=}$.[163] In this case also, the product is isolated only after column chromatography on Florisil.

I. Summary

From the reactions of the germanium hydrides, $PhGeH_3$, R_2GeH_2 (R = Ph, Et, Me), and Ph_3GeH, it is clear that there is a marked tendency, in both photochemical and thermal reactions, for the cleavage of an alkyl or aryl group from the germanium atom. The many types of iron-germanium cluster compounds from mononuclear starting materials make it difficult to predict which compounds will be formed under given reaction conditions. For example, $Ph_2GeFe_2(CO)_8$ forms from the reaction of Ph_3GeH with $Fe_3(CO)_{12}$, but not with $Fe(CO)_5$. It is only an empirical fact that the dimeric compounds $[R_2GeFe(CO)_4]_2$ (R = Et, Ph) form thermally, and are not isolated from the photochemical reactions. The facile thermal and photochemical rearrangement reactions investigated seem to be unique to particular compounds. For example, a digermoxane compound forms from the decomposition of $(Ph_2Ge)_2Fe_2(CO)_7$, but not from the decomposition of $(Et_2Ge)_2Fe_2(CO)_7$. Although no concrete mechanisms can be proposed for the reactions, the profusion of products obtained has increased the knowledge of the chemistry of germanium-iron carbonyl compounds.

TABLE II

INFRARED CARBONYL STRETCHING FREQUENCIES OF IRON-GERMANIUM COMPOUNDS

Compound	Stretching Frequencies,[a,b] cm^{-1}						
$[(Ph_2Ge)_2O]Fe_2(CO)_8$	2095(s)	2047(vs)	2030(s)	2019(vs)	2015(s,sh)	1996(m)	
$(PhGe)_2Fe_3(CO)_9$[c]	2020(s)	1984(m,sh)	1976(m)				
$(EtGe)_2Fe_3(CO)_9$	2016(s)	1980(w)	1967(m)				
$Ph_2GeFe_2(CO)_8$[d]	2093(m)	2044(vs)	2024(m)	2016(s)	2004(w,sh)	1998(m)	1987(w)
$Et_2GeFe_2(CO)_8$	2092(w)	2040(vs)	2023(m)	2009(s)	1997(m)	1986(w)	
$(Ph_2Ge)_2Fe_2(CO)_7$	2061(m)	2034(vs)	2004(s)	1990(m)	1980(w,sh)	1832(m)	
$(Et_2Ge)_2Fe_2(CO)_7$	2054(m)	2023(vs)	1998(s)	1975(s)	1838(m)		
$(PhGeH)_2Fe_2(CO)_7$	2067(w)	2038(vs)	2008(s)	1987(m)	1853(w)		
$[Ph_2GeFe(CO)_4]_2$[d]	2059(m)	2012(m)	2006(m)				
$[Et_2GeFe(CO)_4]_2$[e]	2050	1998	1996	1983			
$(Ph_2Ge)_3Fe_2(CO)_6$[c]	2025(s)	2009(vs)	1976(m)				
$(Et_2Ge)_3Fe_2(CO)_6$	2003(s)	1999(w,sh)	1965(s)				
$(Et_2Ge)_3Fe_2(CO)_6$[c]	2000(s)	1960(m,br)					
$GeFe_4(CO)_{16}$[f]	2012	2048	2074	2031			

TABLE II (continued)

[a] In heptane except as noted.

[b] Key: s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very.

[c] In dichloromethane.

[d] Reference 16, in cyclohexane.

[e] Reference 2, in *n*-hexadecane.

[f] Reference 65, in cyclohexane.

TABLE III

INFRARED STRETCHING FREQUENCIES OF SOLID $[(Ph_2Ge)_2O]Fe_2(CO)_8$[a] BETWEEN 4000 cm^{-1} AND 600 cm^{-1}

Frequency,[b,c] cm^{-1}	Assignment
3060 (w)	C-H stretch
3040 (w)	C-H "
2100-1970 (s-m)	C≡O "
1630 (w)	C=C "
1478 (w)	C-H bend
1426 (m)	C_6H_5 ring deformations[169]
1077 (m)	C_6H_5 " "
993 (w)	C-H bend
794 (m)	Ge-O stretch
729 (m)	C-H bend
693 (m)	C-H bend
602 (m)	Fe-C-O bend or Ge-C stretch

[a] KBr disc.

[b] All strong and medium bands, and weak bands of obvious assignment are listed.

[c] Abbreviations as in Table II.

TABLE IV

MASS SPECTRUM OF $[(Ph_2Ge)_2O]Fe_2(CO)_8$

m/e[a]	Relative Abundance[b,c]	Probable Ion	n
806	3	$[(C_6H_5)_2Ge]_2OFe_2(CO)_n^+$	8
778	8		7
750	6		6
722	41		5
694	203		4
666	35		3
638	85		2
610	505		1
582	380		0
554	360	$[(C_6H_5)_2Ge]_2OFe(CO)^+$	
526	262	$[(C_6H_5)_2Ge]_2OFe^+$	
762	5	$[(C_6H_5)_2Ge]_2Fe_2(CO)_n^+$	7
728	d		6
706	11		5
678	10		4
651[e]	16		3
622	19		2
594	27		1
564	28	$(C_6H_5)_2GeFe_2(CO)_n^+$	8
536	22		7
508	78		6
480	32		5
452	15		4

TABLE IV (continued)

m/e	Relative Abundance	Probable Ion	n
424	82		3
396	133		2
368	87		1
340	174		0
438	505	$(C_6H_5)_4GeFe^+$	
305	872	$(C_6H_5)_3Ge^+$	
284	272	$(C_6H_5)_2GeFe^+$	
262	281	$C_6H_4GeFe_2^+$	
245	107	$(C_6H_5)_2GeOH^+$	
228	734	$(C_6H_5)_2Ge^+$	
206	303	$C_6H_4GeFe^+$	
196	55	$Fe(CO)_5^+$	
168	85	$Fe(CO)_4^+$	
154	514	$(C_6H_5)_2^+$	
151	505	$C_6H_5Ge^+$	
133	377	$C_6H_5Fe^+$	
112	97	$Fe(CO)_2^+$	
84	241	$Fe(CO)^+$	
78	1000	$C_6H_6^+$	
56	596	Fe^+	
28	f	CO^+	

[a] For ions containing one Ge atom, calculated for ^{74}Ge; for two Ge atoms, $^{74}Ge^{72}Ge$.

TABLE IV (continued)

[b] The most intense peak in the spectrum is assigned the value 1000.

[c] Although the relative intensities change slightly with time, so that no two spectra run at the same temperature will be exactly alike, the overall pattern of fragmentation does not change. The spectrum was recorded over a period of eight seconds, at a source temperature of 130°.

[d] Overlapping peaks.

[e] For $[(C_6H_5)_2Ge]_2Fe_2(CO)_3H^+$.

[f] Off scale.

TABLE V

COLOURS AND ANALYTICAL DATA OF IRON-GERMANIUM COMPOUNDS

Compound	Colour	Calculated %		Found %	
		C	H	C	H
$[(Ph_2Ge)_2O]Fe_2(CO)_8$[a]	red	47.7	2.50	47.7	2.28
$(PhGe)_2Fe_3(CO)_9$	purple	35.1	1.40	35.1	1.14
$(Ph_2Ge)_3Fe_2(CO)_6$	purple	52.5	3.15	48.2	3.03
$(Et_2Ge)_3Fe_2(CO)_6$	yellow	32.2	4.50	31.9	4.45
$GeFe_4(CO)_{16}$	red	25.8	0.00	25.8	0.55

[a] For oxygen: Calculated, 17.9; found, 17.6. (Alfred Bernhardt Microanalytisches Laboratorium, West Germany.) Osmometric molecular weight in CH_2Br_2: Calculated, 805; found, 788.

EXPERIMENTAL

GENERAL TECHNIQUES

During all reactions and workup procedures exposure of compounds to air was minimized by use of a nitrogen atmosphere, expecially when compounds were in solution. Sealed tube reactions were carried out using Carius tubes constructed of thick-walled Pyrex tubing, with a volume of about 70 ml. Solid and liquid reagents and solvents were placed directly into the tube, degassed, and frozen in liquid nitrogen before being sealed under vacuum. The reactions were carried out by placing the sealed tube in an oven, whose temperature varied by ±5° from the stated reaction temperature. After reaction the tubes were cooled to room temperature and then to liquid nitrogen temperature before being opened. The gases were allowed to escape and the reaction mixture was transferred to another flask for further workup.

Reactions employing ultraviolet irradiation were carried out with Hanovia lamps (No. L679A, 450 watts, or No. 30620, 140 watts). With the 450 watt apparatus, the slender bulb was place inside a water-cooled quartz jacket. The reaction solution was placed into the annular space between the quartz cooling jacket and an outer Pyrex container. Nitrogen gas was bubbled slowly through the solution via a glass frit at the bottom of the vessel.

The magnetically stirred reaction mixtures were kept below 25° at all times.

With the 140 watt apparatus, the reaction solution was placed inside a slender quartz vessel containing a long, water-cooled cold finger. While stirring magnetically and bubbling nitrogen gas slowly through the mixture, the solution was irradiated with the lamp placed about six inches from the vessel.

It should be noted here that ultraviolet irradiation was employed only for reactions involving $Fe(CO)_5$, while those reactions requiring $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ were carried out using Carius tubes.

Melting points are not given for compounds in this chapter because they decompose slowly over a wide temperature range. (Measurements were taken using a microscope equipped with a Kofler hot stage.) Melting points should therefore not be employed for identification or as a guide to purity. Microanalyses were performed by the microanalytical laboratory of this department, except as noted.

INSTRUMENTATION

Mass spectra were obtained on Associated Electrical Industries MS-9 or MS-12 spectrometers. Samples were introduced on a direct probe, employing the lowest source temperature possible to produce the spectrum (ionizing potential 70 ev). Some mass spectra were interpreted with the aid of a computer program, written in this department by Drs. E. H. Brooks and R. S. Gay and based on original work by Carrick and Glockling,[164] which calculates isotope combination patterns and exact peak masses. An exact mass consists of the weighted average of all isotope combinations involved in the nominal mass. For identification purposes, the sum of the exact isotopic weights of the most abundant isotope combination contained in the nominal mass was sufficiently similar to the average for either value to be used. In all cases calculated and observed patterns were virtually identical.

Proton nmr spectra were recorded on Varian Nuclear Magnetic Resonance Spectrometers, Models A-60 or 56-60A.

Infrared spectra in the carbonyl region were obtained using a Perkin-Elmer Model 337 grating spectrometer equipped with an expanded scale readout accessory and a Hewlett-Packard Model 7127A recorder. The expanded spectra were calibrated with respect to CO band number 31,[165] by introduction of a gas cell containing carbon monoxide at the appropriate time during a continuous run. The band frequencies in wavenumbers were determined using a chart previously calibrated between 2200 and 1800 cm^{-1} with gaseous CO, DCl, and DBr. Deviations between duplicated spectra did not exceed 1 cm^{-1}. Solution spectra were obtained in heptane, hexane, or dichloromethane as noted in Table II, using 0.5 mm path length KBr or NaCl cells.

Infrared spectra in the region 4000 to 600 cm^{-1} were obtained on the Perkin-Elmer Models 337 or 421 spectrophotometers. The sample media for compounds with infrared bands reported in regions other than the carbonyl region are noted in the Tables.

MATERIALS

Reagent grade heptane, hexane, petroleum ether (50-80°), and dichloromethane were distilled under nitrogen from calcium hydride (for hydrocarbons) or phosphorous pentoxide (for CH_2Cl_2), before use. The binary iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were obtained from commercial sources, and were used as supplied.

The chlorogermanium starting materials $PhGeCl_3$, Ph_2GeCl_2, and Et_2GeCl_2were obtained from Alfa Inorganics Inc., Beverly, Mass. Ph_3GeH was obtained from Strem Chemicals Inc., Danvers, Mass. These and all other compounds obtained from commercial sources were used as supplied. For chromatography columns, Florisil (Fisher 100-200 mesh) packed in petroleum ether (bp 50-80°) or heptane was used.

The hydrides $PhGeH_3$, Ph_2GeH_2, and Et_2GeH_2 were synthesized by reduction of $PhGeCl_3$, and Ph_2GeCl_2 in diethyl ether and Et_2GeCl_2 in di-*n*-butyl ether, using $LiAlH_4$. The preparation for Ph_2GeH_2 follows the procedure of Johnson and Harris,[166] but with substitution of Ph_2GeCl_2 for Ph_2GeBr_2 at the reduction stage. There are no published preparations for $PhGeH_3$ and Et_2GeH_2, although reference has been made to their synthesis from the chlorides, and physical data have been given.[167,168]

PROCEDURES

Synthesis of Phenylgermane, $PhGeH_3$

To a suspension of $LiAlH_4$ (7.6 g, 0.20 mol) magnetically stirred in 250 ml diethyl ether was added dropwise over one hour a solution of $PhGeCl_3$ (25.6 g, 0.10 mol) in 50 ml diethyl ether. The mixture was refluxed for 1.5 hours, and then the solvent was gradually replaced by petroleum ether (50-80°) by adding 300 ml of the hydrocarbon in three stages. After each stage 100 ml of solvent was distilled off, until a total of 300 ml of solvent was removed. The solution was filtered and the remaining solvent was distilled off. The crude product was distilled at 40 mm pressure over a boiling range of 70-72°, affording 7.2 g, 50% yield, of $PhGeH_3$. An nmr spectrum of the neat liquid showed only the absorptions expected for the product.

Synthesis of Diethylgermane, Et_2GeH_2

To a suspension of $LiAlH_4$ (3.0 g, 0.079 mol) magnetically stirred in 30 ml di-*n*-butyl ether was added dropwise over 45 minutes a solution of Et_2GeCl_2 (25 g, 0.12 mol) in 50 ml di-*n*-butyl ether. After stirring for one more hour, the product was fractionally distilled at about 700 mm pressure. A total of 10.2 g, 62% yield, of Et_2GeH_2 was collected over a boiling range of 70-79°. From an nmr spectrum of the neat liquid, the product was estimated to be about 95% pure.

Reaction Between Diphenylgermane and Iron Pentacarbonyl

A solution of iron pentacarbonyl (0.75 ml, 5.6 mmol) and diphenylgermane (1.5 g, 6.6 mmol) in 200 ml heptane was irradiated with the 450 watt source for about 40 hours. During the irradiation the progress of the reaction was monitored by taking samples of the solution for infrared spectra. After 40 hours irradiation, little iron pentacarbonyl remained. The dark brown heptane solution was filtered through a glass frit (solution A) and the solids remaining on the filter and in the reaction vessel were dissolved in dichloromethane and also filtered (solution B).

Solution B was concentrated on a rotary evaporator to about 20 ml, and cooled in a dry ice-acetone bath overnight. About 75 mg of purple $(Ph_2Ge)_3Fe_2(CO)_6$ crystallized on cooling, and spectral and analytical results were obtained without further purification.

Solution A was concentrated to about 10 ml on a rotary evaporator and then carefully chromatographed on a column of Florisil packed in heptane. Of the seven coloured bands visible on the column during the elution only the three principal bands yielded products which could be isolated and shown to contain iron-germanium bonds. The first two bands, orange and blue-green, eluted with heptane, were identified by infrared spectra as $Fe(CO)_5$ and $Fe_3(CO)_{12}$, respectively. The third band, yellow, eluted with a 2:1 mixture of heptane:dichloromethane, was shown by mass and infrared spectra to be $Ph_2GeFe_2(CO)_8$.

The fourth band, purple, was eluted with a 1:2 mixture of heptane:dichloromethane, and the solution reduced to dryness on a rotary evaporator. The residue was dissolved in a minimum amount of heptane, and the solution was cooled to -78°. The yield of pure $(PhGe)_2Fe_3(CO)_9$ was about 50 mg.

Following the purple band was a broad, light green zone, and then a very narrow red-brown band of a highly air sensitive, unidentified compound. The solution of the final yellow band, eluted with dichloromethane, was evaporated to dryness and the residue was dissolved in a minimum amount of heptane to give a very deep yellow solution. Cooling in the refrigerator at -20° yielded about 150 mg of $[(Ph_2Ge)_2O]Fe_2(CO)_8$.

If, instead of being chromatographed immediately on Florisil, solution A is allowed to stand in the refrigerator at -5° for at least two weeks, large red crystals of $(Ph_2Ge)_2Fe_2(CO)_7$ sometimes form. This compound was identified by mass and infrared spectra to be the same compound obtained previously from a sealed tube reaction.[16] The conditions which promote crystal formation in some cases, but not in others, are not understood.

Reaction Between Diethylgermane and Iron Pentacarbonyl

The same general procedure as with Ph_2GeH_2 was used. Iron pentacarbonyl (0.40 ml, 3.0 mmol) and diethylgermane (0.53 g, 4.0 mmol) in 200 ml heptane were irradiated with the 450 watt source for about 20 hours, at the end of which little iron pentacarbonyl remained. The solution was concentrated under reduced pressure and then chromatographed on a column of Florisil packed in heptane. Three intensely coloured bands, yellow, purple, and yellow, were eluted with heptane. All three coloured solutions were reduced in volume and cooled in the refrigerator at -20°. The first yellow band produced about 0.2 g, 20% based on germanium, of $(Et_2Ge)_3Fe_2(CO)_5$, identified by infrared and mass spectra and microanalysis.

The purple solution gave a very small amount of dark red solid, whose infrared and mass spectra identified it as $(EtGe)_2Fe_3(CO)_9$.

The second yellow band after concentration gave no solid on cooling to -78°, and on removal of all solvent, left an orange oil mixed with brown solid material. Attempted sublimation at room temperature *in vacuo* gave an orange oil and a brown film, the latter likely due to decomposition, on the cold finger. Nevertheless, infrared and mass spectra led to a formulation analogous to $(Ph_2Ge)_2Fe_2(CO)_7$. The mass spectrum exhibited a molecular ion and the expected fragmentation pattern for $(Et_2Ge)_2Fe_2(CO)_7$.

Reaction Between Diethylgermane and Triiron Dodecacarbonyl

A Carius tube containing diethylgermane (0.53 g, 4.0 mmol) and triiron dodecacarbonyl (2.0 g, 4.0 mmol) in 10 ml hexane was heated for 16 hours at 90°, and then 3 hours at 120°. After opening the tube, the dark orange reaction mixture and hexane extracts of the residual solid material were filtered and the filtrate was concentrated under reduced pressure. Cooling to -78° afforded pale green $[Et_2GeFe(CO)_4]_2$ (0.4 g, 35% based on germanium), identified spectroscopically and microanalytically as the compound originally synthesized by Kahn and Bigorgne.[2] The mother liquor was concentrated further and chromatographed on Florisil, using heptane as eluent. The infrared spectrum of the first broad, yellow band showed a mixture of two compounds. Cooling of this solution after concentration yielded about 0.2 g (20% based on germanium) of $(Et_2Ge)_3Fe_2(CO)_6$. Sublimation of the residue from this crystallization gave a yellow oil, identified by infrared and mass spectra as $Et_2GeFe_2(CO)_8$. Repeated sublimations and attempts at crystallization were not successful in removing impurity bands in the infrared spectrum of this compound.

The last band from the Florisil column consisted of $(Et_2Ge)_2Fe_2(CO)_7$, and as with $Et_2GeFe_2(CO)_8$, a sample suitable for microanalysis was not obtained.

Reaction Between Diethylgermane and Diiron Enneacarbonyl

A Carius tube containing diethylgermane (0.53 g, 4.0 mmol) and diiron enneacarbonyl (1.45 g, 4.0 mmol) in 10 ml heptane was heated at 90° for 18 hours. After opening the tube, an infrared spectrum of the reaction mixture showed mostly iron pentacarbonyl. After removing heptane and $Fe(CO)_5$ *in vacuo*, recrystallization of the oil from a small amount of heptane at -78° produced a mixture of crystalline and amorphous solids, the infrared spectrum of which showed three previously isolated compounds, $(Et_2Ge)_2Fe_2(CO)_7$, $Et_2GeFe_2(CO)_8$, and $[Et_2GeFe(CO)_4]_2$. There were no CO absorption bands for $(Et_2Ge)_3Fe_2(CO)_6$. Since these compounds were characterized in the previous reactions, the mixture of solids was not chromatographed for purification.

Reaction Between Phenylgermane and Iron Pentacarbonyl

The same general procedure as with Ph_2GeH_2 was used. Iron pentacarbonyl (0.81 ml, 6.0 mmol) and phenylgermane (0.4 g, 2.6 mmol) in 200 ml heptane were irradiated with the 450 watt source for 11 hours. The solution was concentrated under reduced pressure and then chromatographed on a column of Florisil. A broad yellow band eluted with varying mixtures of heptane and dichloromethane was collected in several fractions. There were small regions of red, green, and brown bands within the yellow band, but all fractions showed as the main product $GeFe_4(CO)_{16}$, by infrared spectra. All fractions were reduced in volume and cooled to -20° in the refrigerator, to afford a total of about 0.1 g (20% based on iron) of red $GeFe_4(CO)_{16}$. None of the fractions afforded solids due to the other compounds visible on the chromatography column on further attempts at crystallization.

Reaction Between Phenylgermane and Diiron Enneacarbonyl

Phenylgermane (0.30 g, 2.0 mmol), diiron enneacarbonyl (0.73 g, 2.0 mmol) and heptane (8 ml) were sealed in a Carius tube and heated at 70° for 40 hours. After opening the tube the heptane solution was poured out and the remaining solids extracted with dichloromethane. Solvent and $Fe(CO)_5$ from the combined solutions were removed *in vacuo*, and recrystallization of the remaining oil from a dichloromethane-heptane mixture gave impure yellow crystals of $(PhGeH)_2Fe_2(CO)_7$. Repeated attempts at recrystallization or sublimation to obtain a sample pure enough for microanalysis afforded oils or microcrystalline material, both visibly contaminated with impurities.

Reaction Between Phenylgermane and Triiron Dodecacarbonyl

A Carius tube containing phenylgermane (0.60 g, 3.9 mmol) and triiron dodecacarbonyl (1.0 g, 2.0 mmol) in

6 ml heptane was heated for 36 hours at 65°. After cooling and opening the tube, the contents were washed out with heptane and dichloromethane. The solvents from the combined washings were removed at reduced pressure and excess $Fe_3(CO)_{12}$ was sublimed off. The residue in dichloromethane was chromatographed on Florisil, affording a broad, yellow band, eluted with heptane and then dichloromethane, and collected in several fractions. Infrared spectra of these fractions showed the presence of $(PhGeH)_2Fe_2(CO)_7$ and $GeFe_4(CO)_{16}$, in varying ratios. Since the amounts obtained from this reaction were rather small and both compounds had been isolated from the previous reactions, no further attempt was made at separation of the two products.

Reaction Between Triphenylgermane and Iron Pentacarbonyl

A solution of triphenylgermane (0.80 g, 2.7 mmol) and iron pentacarbonyl (4.0 ml, 3.0 mmol) in 100 ml heptane was irradiated with the 140 watt source for 20 hours. After removal of heptane and unreacted $Fe(CO)_5$ under reduced pressure, an infrared spectrum of the remaining oil showed the presence of only two compounds, $(Ph_2Ge)_2Fe_2(CO)_7$ and $[(Ph_2Ge)_2O]Fe_2(CO)_8$. Crystallization of the oil, after dissolving into heptane, over a period of about three weeks at -5° gave 0.12 g (10% based on germanium) of the digermoxane compound.

Reaction of Triphenylgermane and Triiron Dodecacarbonyl

A Carius tube was charged with triphenylgermane (0.80 g, 2.7 mmol), triiron dodecacarbonyl (0.5 g, 0.9 mmol), and heptane (10 ml), and heated for 36 hours at 75°. After cooling and opening the tube, heptane and iron pentacarbonyl were removed at reduced pressure. The resulting oil was chromatographed on a column of Florisil, using heptane as eluent. Only one coloured band emerged from the column, a yellow solution of $Ph_2GeFe_2(CO)_8$.

Reaction of Disodium Octacarbonyl Diferrate(-II) with Diphenyldichlorogermane

Disodium octacarbonyl diferrate(-II), $Na_2[Fe_2(CO)_8]$, was prepared by the method of Ruff[58] using $Fe(CO)_5$ (0.70 ml, 5.2 mmol) and sodium amalgam (25 g, 1%) in THF (50 ml), irradiating with the 140 watt source. After four hours, the THF solution containing $Na_2[Fe_2(CO)_8]$ was decanted, and diphenyldichlorogermane (0.71 g, 2.4 mmol) was added. After stirring for one hour the solvent was removed under reduced pressure and the oily residue chromatographed on Florisil. The two yellow solutions eluted with heptane consisted of $Fe(CO)_5$ and a small amount of $Ph_2GeFe_2(CO)_8$, respectively, as shown by infrared spectra. The amount of solid $Ph_2GeFe_2(CO)_8$ obtained was insufficient to allow recrystallization for an analytical sample.

Photochemical Decomposition of Bis-μ-diphenylgermanium-bis-(tetracarbonyliron)

Toluene (50 ml) and a small amount of $[Ph_2GeFe(CO)_4]_2$ (c. 0.1 g), prepared from $Na_2[Fe(CO)_4]$ and Ph_2GeCl_2 in THF,[64] were placed in a small quartz vessel which was immersed in a dry ice-acetone bath contained in an unsilvered quartz dewar. The solution was irradiated with the 140 watt source for four hours, with the reaction temperature kept about -78°. After irradiation an infrared spectrum in toluene showed greater than 50% conversion to $(Ph_2Ge)_2Fe_2(CO)_7$ (estimated from infrared intensities). Warming to room temperature and removal of toluene resulted in a yellow oil, whose infrared spectrum in heptane showed almost complete conversion to $[(Ph_2Ge)_2O]Fe_2(CO)_8$.

CHAPTER III

SYNTHESIS AND PROPERTIES OF SOME GERMANIUM AND TIN DERIVATIVES OF THE η-(CYCLOPENTADIENYL)TRICARBONYLS OF MANGANESE AND RHENIUM

INTRODUCTION

The first group IV metal derivative containing a $CpM(CO)_2$* moiety was *cis*-$CpMn(CO)_2(SiCl_3)H$, reported in 1969.[170] Since then the number of group IV derivatives of this type has been quite limited, consisting mainly of silicon complexes. As can be seen from the list of silicon, germanium, and tin derivatives of $CpM(CO)_3$ in Table VI, only one such germanium compound was known up to the time of the present work.

Initial interest in compounds of this type grew from the extension of synthetic methods for group IV metal-transition metal carbonyl compounds by the oxidative elimination of carbon monoxide by R_3EH (E = Si, Ge, or Sn). The versatility of trichlorosilane in oxidative elimination reactions with transition metals varying from chromium to cobalt was demonstrated in 1969.[170]

Interest in transition metal-group IV metal hydrides was intensified when an X-ray structural study[174] of

*In this chapter, M refers to Mn and Re, E refers to Ge and Sn, unless otherwise stated.

TABLE VI

GROUP IV METAL DERIVATIVES OF CpM(CO)$_3$

Compound	Abbreviations	References
cis-CpMn(CO)$_2$(SiCl$_3$)H[a]		41,170
cis-CpMn(CO)$_2$(SiCl$_2$Ph)H		228
cis-CpMn(CO)$_2$(SiPh$_2$H)H		171
cis-CpMn(CO)$_2$(SiPh$_3$)H[b]		41,171
cis-CpMn(CO)$_2$(GePh$_3$)H		‡
[Et$_3$NH][CpMn(CO)$_2$SiCl$_3$]		172
[Et$_4$N][CpMn(CO)$_2$SiCl$_3$]		172
[Ph$_4$As][CpMn(CO)$_2$ECl$_3$][b]		173
trans-CpMn(CO)$_2$(GePh$_3$)$_2$		‡
trans-CpMn(CO)$_2$(ECl$_3$)$_2$		‡
trans-CpMn(CO)$_2$(SiCl$_3$)(SnCl$_3$)[b]		172
trans-(MeC$_5$H$_4$)Mn(CO)$_2$(SiCl$_3$)(SnCl$_2$Ph)		172
trans-(MeC$_5$H$_4$)Mn(CO)$_2$(SiCl$_3$)(SnClPh$_2$)		172
trans-[(MeC$_5$H$_4$)Mn(CO)$_2$(SiCl$_3$)]$_2$SnCl$_2$		172
CpRe(CO)$_2$(SiR$_3$)H[a,c]	R = Ph, CH$_2$Ph	171
cis-CpRe(CO)$_2$(SiHPh$_2$)H		171
CpRe(CO)$_2$(SiCl$_3$)H[c,d]		171
trans-CpRe(CO)$_2$(GeX$_3$)H[a]	X = Cl, Br	‡
trans-CpRe(CO)$_2$(SnCl$_3$)H		‡
[Et$_4$N][CpRe(CO)$_2$(SiPh$_3$)]		171
[Et$_4$N][CpRe(CO)$_2$(GeX$_3$)]	X = Cl, Br	‡
[Et$_4$N][CpRe(CO)$_2$(SnCl$_3$)]		‡
trans-CpRe(CO)$_2$(GeCl$_3$)X	X = Cl, Br, I	‡

TABLE VI (continued)

Compound	Abbreviations	References
trans-$\mathrm{CpRe(CO)_2(GeBr_3)Br}$		‡
trans-$\mathrm{CpRe(CO)_2(SnCl_3)Cl}$		‡
trans-$\mathrm{CpRe(CO)_2(GeCl_3)R}$	R = Me, Et[d]	‡
trans-$\mathrm{CpRe(CO)_2[Ge(OR)Cl_2]Cl}$	R = Me, Et	‡
trans-$\mathrm{CpRe(CO)_2(GeCl_3)_2}$		‡
trans-$\mathrm{CpRe(CO)_2(GeCl_2Et)_2}$[d]		‡
trans-$\mathrm{CpRe(CO)_2(SnPh_3)_2}$		‡
trans-$\mathrm{CpRe(CO)_2(EPh_3)Me}$	E = Si, Ge[d]	‡,171
trans-$\mathrm{CpRe(CO)_2(SiPh_3)(SnMe_3)}$		171
trans-$\mathrm{CpRe(CO)_2(SiPh_3)I}$		171
trans-$\mathrm{CpRe(CO)_2[Si(CH_2Ph)_3]Me}$		171

[a] Also the deuteride.

[b] Also the $(\mathrm{MeC_5H_4})$ analogue.

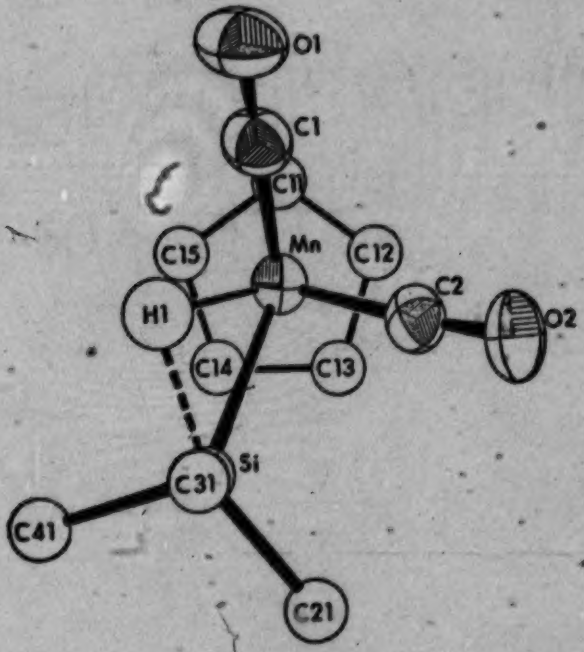
[c] *Cis* and *trans* isomers.

[d] Characterized by infrared and mass spectra only.

‡ Compound prepared in this work.

cis-CpMn(CO)$_2$(SiPh$_3$)H located the hydride ligand at a normal covalent bond distance from the manganese atom (1.55 Å) but close enough to the silicon atom (1.76 Å) to imply some degree of bonding interaction (Fig. 12). More recent structural studies on *cis*-CpMn(CO)$_2$(SiCl$_2$Ph)H[175] and *cis*-CpRe(CO)$_2$(SiPh$_3$)H[176] also indicated short silicon-hydrogen distances (1.79 and c. 2.2 Å, respectively).

Furthermore, although the transition metal-hydrogen stretching vibrations are expected to be



Molecular Structure of *cis*-CpMn(CO)$_2$(SiPh$_3$)H

Phenyl rings omitted for clarity.

Mn-Si = 2.424(2) Å
Mn-H = 1.55(4)
Si-H = 1.76(4)

Figure 12

infrared active, no bands assignable to such vibrations were detected in infrared spectra of the transition metal silyl hydride complexes listed in Table VI with the exceptions of *cis*-$\mathrm{CpMn(CO)_2(SiCl_3)H}$[41] and *cis*-$\mathrm{CpMn(CO)_2(SiCl_2Ph)H}$,[228] where bands at 1887 and 1895 $\mathrm{cm^{-1}}$, respectively, were assigned to ν(Mn-H). The band at 1887 $\mathrm{cm^{-1}}$ was shifted down to 1355 $\mathrm{cm^{-1}}$ in the spectrum of the deuteride. In contrast, solid state Raman spectra of these compounds located stretching modes in the expected transition metal hydride stretching region, with the metal-deuteride frequencies at corresponding lower energy.[171]

A study of the kinetics and mechanism of displacement of silane from *cis*-$\mathrm{CpM(CO)_2(SiR_3)H}$ (M = Mn, R = Ph, Cl; M = Re, R = Ph) by triphenylphosphine was consistent with an initial unimolecular rate-determining step involving dissociation of a silane molecule:[62]

$$\mathrm{CpM(CO)_2(SiR_3)H} \longrightarrow [\mathrm{CpM(CO)_2}] + \mathrm{HSiR_3} \xrightarrow{\mathrm{Ph_3P}} \mathrm{CpM(CO)_2Ph_3P} + \mathrm{HSiR_3} \qquad \text{(III-1)}$$

The activation energy for silane dissociation was much lower for R = Ph than for R = Cl. Whether this difference in reactivity had any relation to the H···Si interaction found in the solid state structures, or any connection with the lack of infrared M-H stretching bands was an unsettled question.

In view of the above physical and chemical observations on $CpM(CO)_2(SiR_3)H$ complexes, it seemed desirable to synthesize some corresponding germanium derivatives and to compare their properties with the silicon analogues.

In the Results and Discussion, Part A will deal with the attempted formation of manganese and rhenium hydrides using germanes of the form R_3GeH. Part B will include the synthesis of anions of the form $[CpM(CO)_2EX_3]^-$ (X = Cl, Br) and their protonation and deuteration. Part C will discuss reactions of these rhenium and manganese anions with alkylhalosulphonates, and Part D will then cover all other derivatives of $CpM(CO)_3$. Discussions of the infrared, nmr, and mass spectra will be given in appropriate sections within each Part.

RESULTS AND DISCUSSION

A. Reactions of R_3GeH and Ph_3SnH with $CpM(CO)_3$ (R_3 = Ph_3, $PhCl_2$, $EtCl_2$, and Cl_3)

1. Reactions with Cl_3GeH

The photochemical reactions of Cl_3SiH with $CpM(CO)_3$ afforded the *cis*-trichlorosilyl metal hydrides:[41,171]

$$CpM(CO)_3 + Cl_3SiH \rightarrow cis\text{-}CpM(CO)_2(SiCl_3)H + CO \qquad (III\text{-}2)$$

The corresponding reactions of $CpM(CO)_3$ with Cl_3GeH did *not* give *cis*-trichlorogermyl analogues. (Isomers were differentiated by infrared spectroscopy; see section 4.)

In the case of $CpMn(CO)_3$, very little reaction occurred without ultraviolet irradiation, and even with prolonged irradiation and a large excess of Cl_3GeH, only a low yield of *trans*-$CpMn(CO)_2(GeCl_3)_2$ was isolated, and no hydride of the form $CpMn(CO)_2(GeCl_3)H$ was detected. Under these photolytic conditions, the first step in the mechanism would probably be dissociation of a carbonyl ligand:

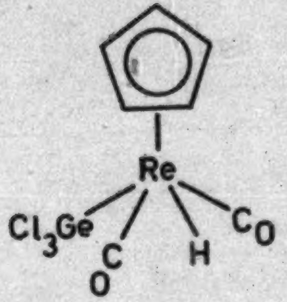
$$CpMn(CO)_3 \xrightarrow{h\nu} [CpMn(CO)_2]^* + CO \qquad (III\text{-}3)$$

In reactions where this photolysis takes place in coordinating solvents such as THF, the electronically unsaturated species is believed to be stabilized by coordination of a solvent molecule.[177] A study of the photolysis of methylcyclohexane-nujol glasses containing $CpMn(CO)_3$ at 80° K led to an assignment of CO stretching bands to the unsaturated species $[CpMn(CO)_2]$ in the infrared spectrum.[178] In the reaction with Cl_3GeH, this unsaturated species could recombine with CO in the reverse of reaction III-3, or could combine with germanium species to lead to the product, *trans*-$CpMn(CO)_2(GeCl_3)_2$.

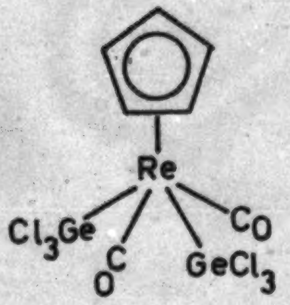
$$[CpMn(CO)_2]^* + 2Cl_3GeH \rightarrow trans\text{-}CpMn(CO)_2(GeCl_3)_2 + H_2 \qquad \text{(III-4)}$$

Although the only bands in the infrared spectra of the reaction mixtures were those of $CpMn(CO)_3$ and *trans*-$CpMn(CO)_2(GeCl_3)_2$, the hydride, $CpMn(CO)_2(GeCl_3)H$ would be a logical intermediate.

In contrast to the preparation of *trans*-$CpMn(CO)_2(GeCl_3)_2$, the room temperature reaction of Cl_3GeH with $CpRe(CO)_3$ in the dark occurred within minutes, if an excess of the germane was used. An infrared spectrum taken immediately after combining the reactants showed the presence of two compounds, *trans*-$CpRe(CO)_2(GeCl_3)H$, **25**, and *trans*-$CpRe(CO)_2(GeCl_3)_2$, **26**. After one hour, only bands due to **26** remained in the spectrum. At 0° and with a slight excess of $CpRe(CO)_3$, only about 40 percent of the tricarbonyl (estimated from infrared spectra) had reacted after four hours, and there was a much larger amount of the bis(trichlorogermyl) compound



25



26

than the hydride. If **25** is an intermediate in the formation of **26**, then any unreacted Cl_3GeH must preferably combine with **25** (III-5) than with the tricarbonyl (III-6). It would seem therefore that the activation energy for the reaction leading to **25** must be greater than that leading to **26**.

trans-$CpRe(CO)_2(GeCl_3)H$ + Cl_3GeH → *trans*-$CpRe(CO)_2$-$(GeCl_3)_2$ + H_2 (III-5)

$CpRe(CO)_3$ + Cl_3GeH → *trans*-$CpRe(CO)_2(GeCl_3)H$ + CO (III-6)

In a separate experiment, the hydride, **25**, prepared by another route (see Part B), reacted with Cl_3GeH (under the same conditions) to produce **26**.

It should be noted that there was no evidence for the formation of the *cis* isomer of **25** in reaction III-6 or *cis*-$CpMn(CO)_2(GeCl_3)H$ in reaction III-4. Non-isolation of the *cis* hydrides, if indeed such species are formed, could be due to a tendency for the dissociation of germane from such species (III-7), similar to the first step in

$$cis\text{-}CpM(CO)_2(GeCl_3)H \rightarrow [CpM(CO)_2]^* + Cl_3GeH \quad (III\text{-}7)$$

reaction (III-1). However, the fact that the activation energy for silane dissociation in III-1 was greater for the trichlorosilyl complex than for the triphenylsilyl complex does not support this speculation. (*cis*-$CpMn(CO)_2(GePh_3)H$ has been found to be a stable compound; see section 2.)

For the manganese reaction, which is photochemically initiated, this non-isolation should be contrasted with the formation *cis*-$CpMn(CO)_2(GeCl_3)H$ by a non-photolytic method (see Part B, section 2). Moreover, the facile loss of HCl from this molecule in the mass spectrometer suggests another possibility for decomposition under photolytic conditions. However, there exists no direct evidence for this speculation, and other principles may be the determining factors in the non-isolation and possible non-formation of the *cis*-trichlorogermyl hydrides of manganese and rhenium.

The extended ultraviolet irradiation of a solution of $C_6H_6Cr(CO)_3$ with an excess of Cl_3GeH afforded as the only product the bis(trichlorogermyl) compound in good yield:

$$C_6H_6Cr(CO)_3 + 2Cl_3GeH \rightarrow trans\text{-}C_6H_6Cr(CO)_2(GeCl_3)_2 + CO + H_2 \quad (III\text{-}8)$$

Here, as in the $CpMn(CO)_3$ reaction to form *trans*-$CpMn(CO)_2$-$(GeCl_3)_2$, one would expect the photolytically produced unsaturated complex $[C_6H_6Cr(CO)_2]^*$ to react in some way with two molecules of Cl_3GeH to form the product, possibly having as an intermediate the hydride which would form through oxidative elimination.

The fact that reaction III-6 and that reaction leading to *trans*-$CpRe(CO)_2(GeCl_3)_2$ occur in the dark, whereas the manganese and chromium derivatives must be photochemically produced, suggests that unimolecular loss of CO from $CpRe(CO)_3$ is not a major step in the mechanism. It seems likely that there may be some facile interaction between $CpRe(CO)_3$ and Cl_3GeH that induces the reactions to proceed. As mentioned in Chapter I, there is evidence that divalent $GeCl_2$ exists in equilibrium with Cl_3GeH (I-28). It has been suggested that the equilibrium is shifted to the right in solvents such as diethyl ether; however, the formation of 25 and 26 occurs in heptane, in which the dissociation of Cl_3GeH is less likely to occur. Whether $CpRe(CO)_3$ is initially attacked by $GeCl_2$, or even H^+ or $GeCl_3^-$, the fact remains that the same mode of attack does not occur to any visible extent in the cases of $CpMn(CO)_3$ or $C_6H_6Cr(CO)_3$.

An infrared study[179,180] of the protonation of arene or cyclopentadienyl metal complexes by either hydrogen chloride or trifluoroacetic acid in dichloromethane has shown that the basicity of the metal atom increases in the series

$CpMn(CO)_2L < C_6H_6Cr(CO)_2L < CpRe(CO)_2L$, L = CO or tertiary phosphine.

If the initial step in the formation of *trans*-$CpRe(CO)_2(GeCl_3)H$ were protonation, then $CpRe(CO)_3$ would be expected to react most readily, as it does. By extending this hypothesis, one might expect the reaction of $CpRe(CO)_3$ and $SnCl_2$ in the presence of hydrogen chloride to produce the analogous tin complex. However, in dichloromethane there was no evidence of any carbonyl-containing substance other than $CpRe(CO)_3$.

2. Reactions with Ph_3GeH and Ph_3SnH

Whereas the photochemical reaction between Ph_3SiH and $CpRe(CO)_3$ led directly to *cis*-$CpRe(CO)_2(SiPh_3)H$,[171] no trace of any germanium-containing rhenium carbonyl derivative could be found on reaction of Ph_3GeH with $CpRe(CO)_3$ under either photochemical and/or thermal conditions. Indeed, no new carbonyl-containing species were shown by infrared spectra of reaction mixtures, and only slow decomposition of $CpRe(CO)_3$ occurred.

Prolonged ultraviolet irradiation of $CpRe(CO)_3$ in the presence of excess Ph_3SnH produced a very small amount of *trans*-$CpRe(CO)_2(SnPh_3)_2$ as the only product.

The photochemical reactions of $CpMn(CO)_3$ with Ph_3GeH yielded two products, *cis*-$CpMn(CO)_2(GePh_3)H$ and *trans*-$CpMn(CO)_2(GePh_3)_2$. The hydride was prepared by reaction of equimolar amounts of the two starting materials under ultraviolet light, during which an equimolar amount of gas was evolved from the solution. Attempted deprotonation of *cis*-CpMn(CO)$_2$(GePh$_3$)H with triethylamine gave no reaction, and with methanolic potassium hydroxide no carbonyl-containing compound was detected after removal of the methanol. The bis(triphenylgermyl) derivative, *trans*-CpMn(CO)$_2$(GePh$_3$)$_2$, was produced in very low yield from a reaction involving a 2:1 mole ratio of germanium to manganese starting materials.

Similar reactions of CpMn(CO)$_3$ with Ph$_3$SnH did not afford any isolable products. Although a pair of bands assignable to *cis*-CpMn(CO)$_2$(SnPh$_3$)H was observed in infrared spectra of reaction mixtures, unreacted CpMn(CO)$_3$ was the predominant species throughout the irradiation. No solid material containing the new bands was obtained on workup of the reactions.

In contrast to the reactions with Ph$_3$SiH, there seems to be no pattern in the reactions of Ph$_3$GeH and Ph$_3$SnH with CpM(CO)$_3$. With present knowledge there do not seem to be any clear bonding or mechanistic explanations for these differences in behavior.

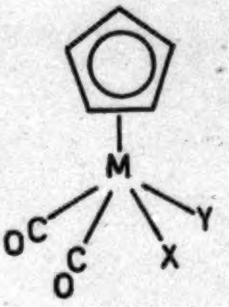
3. Reactions with other monofunctional germanes

Because of the dissimilarity of the trichloro- and triphenyl-germane reactions, PhCl$_2$GeH and EtCl$_2$GeH were synthesized and reacted with CpRe(CO)$_3$. Ultraviolet irradiation with PhCl$_2$GeH gave essentially no reaction, as indicated by infrared spectra of the reaction mixture. With $EtCl_2GeH$ the same conditions produced a very small amount of oily solid, characterized by infrared and mass spectrometry as *trans*-$CpRe(CO)_2(GeCl_2Et)_2$. These two reactions seem to indicate that the facile reaction between Cl_3GeH and $CpRe(CO)_3$ is due to a peculiarity in Cl_3GeH that is absent in its RCl_2GeH analogues.

The photochemical reaction between $CpRe(CO)_3$ and Ph_3GeLi led to the formation of a very small amount of $Li[CpRe(CO)_2GePh_3]$, as estimated from the very low yield of *trans*-$CpRe(CO)_2(GePh_3)Me$ on addition of MeI. This reaction was not reproducible, and all attempts to make other derivatives from $Li[CpRe(CO)_2GePh_3]$ were unsuccessful.

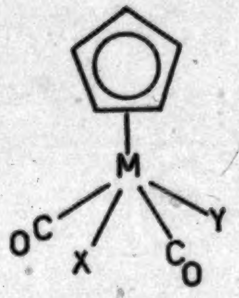
4. Infrared and mass spectra and stereochemistry

The assignment of *cis* or *trans* configuration for complexes of the type $CpM(CO)_2XY$ is based mainly on relative intensities of carbonyl stretching vibrations in the infrared spectra. The arrangement of the five ligands about the central metal can be loosely viewed as forming a "square pyramidal" structure with the cyclopentadienyl ring forming the apex and X, Y, and the two CO ligands forming the four-cornered base:



cis

27a



trans

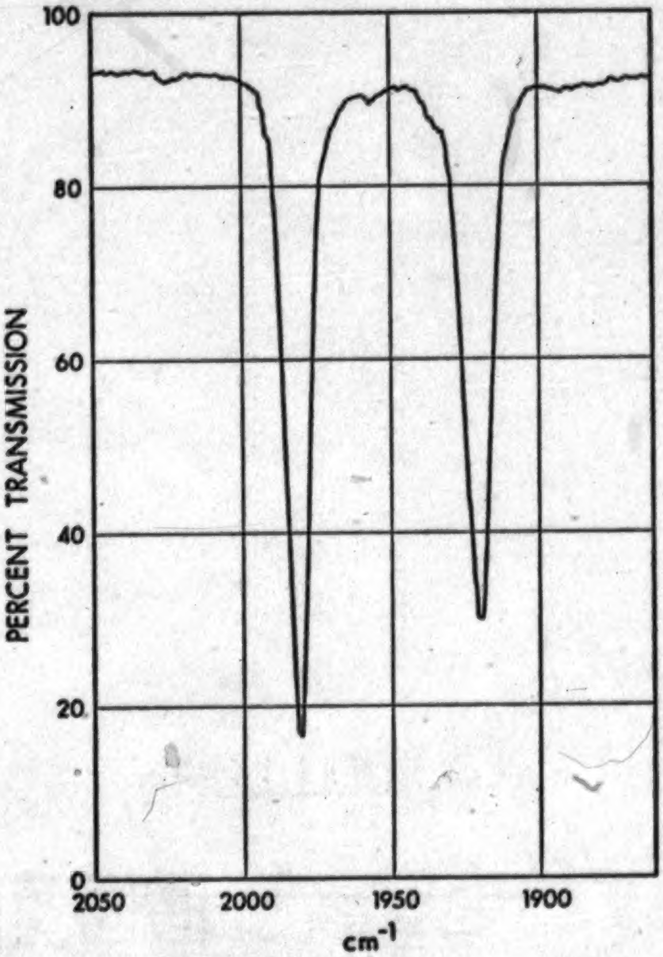
27b

Early work[181-183] on cyclopentadienyl tungsten and molybdenum compounds suggested that complexes with a more intense high energy, symmetric, CO stretching band have the *cis* arrangement, **27a**, while those with a more intense low energy, antisymmetric, CO stretching band have a *trans* configuration, **27b**. Further studies have confirmed the distinction between *cis* and *trans* isomers by the use of ^1H, ^{13}C, and ^{31}P nmr on compounds such as $CpMo(CO)_2(PMe_2Ph)X$[184] and $CpW(CO)_2L(SnMe_3)$[185] (X = Cl, Br, I; L = tertiary phosphine or phosphite).

Final confirmation came from X-ray structural studies of *trans*-$CpMo(CO)_2I(PPh_3)$[186] and *cis*-$CpMn(CO)_2(SiPh_3)H$,[174] both of which showed the expected relative intensities of CO stretching bands in the solution infrared spectra. Infrared intensity measurements have also been used for calculation of the angles between CO vibrators in metal dicarbonyl compounds such as $CpW(CO)_2S_2CNMe_2$[187] and B(1-pyrazolyl)$_4$Mn$(CO)_2PPh_3$.[83]

It has been found that all manganese hydrides of the form $CpMn(CO)_2(SiR_3)H$ (R = H, Ph, Cl) exist only as *cis* isomers.[171,174,188] In the present work $CpMn(CO)_2(GePh_3)H$ also exists only as the *cis* isomer, as shown by the infrared spectrum (Fig. 13). The rhenium hydrides, $CpRe(CO)_2$-$(SiR_3)H$ (R = Ph, $CH_2C_6H_5$), have been found to form both *cis* and *trans* isomers, but under different conditions.[171] For the hydride with R = $CH_2C_6H_5$, both isomers formed in the oxidative elimination reaction involving $CpRe(CO)_3$ and $(C_6H_5CH_2)_3SiH$. For R = Ph, the *cis* isomer and only a trace amount of *trans* formed in the corresponding reaction. The *trans* isomer was formed exclusively from the protonation of $[Et_4N][CpRe(CO)_2SiCl_3]$ by phosphoric acid. In this work, as has been noted for $CpRe(CO)_2(GeCl_3)H$ (and also for $CpRe(CO)_2(GeBr_3)H$ and $CpRe(CO)_2(SnCl_3)H$, (*vide infra*), only the *trans* isomers are formed. These variations in stereochemistry seem to reflect a situation where the major determining factors for stereochemistry are the size of the group IV ligand and perhaps the bond length to the transition metal. A *cis* structure will be formed only if the stereochemical reqirements of the group IV ligand are not too large. Certainly in the compounds containing two $GeCl_3$ or $GePh_3$ groups a *cis* structure would be sterically prohibited. X-ray crystal structures of similar *cis* and *trans* complexes would be helpful in clarifying this situation.

Infrared bands of bis(trihalo-group IV) derivatives



cis-CpMn(CO)$_2$(GePh$_3$)H

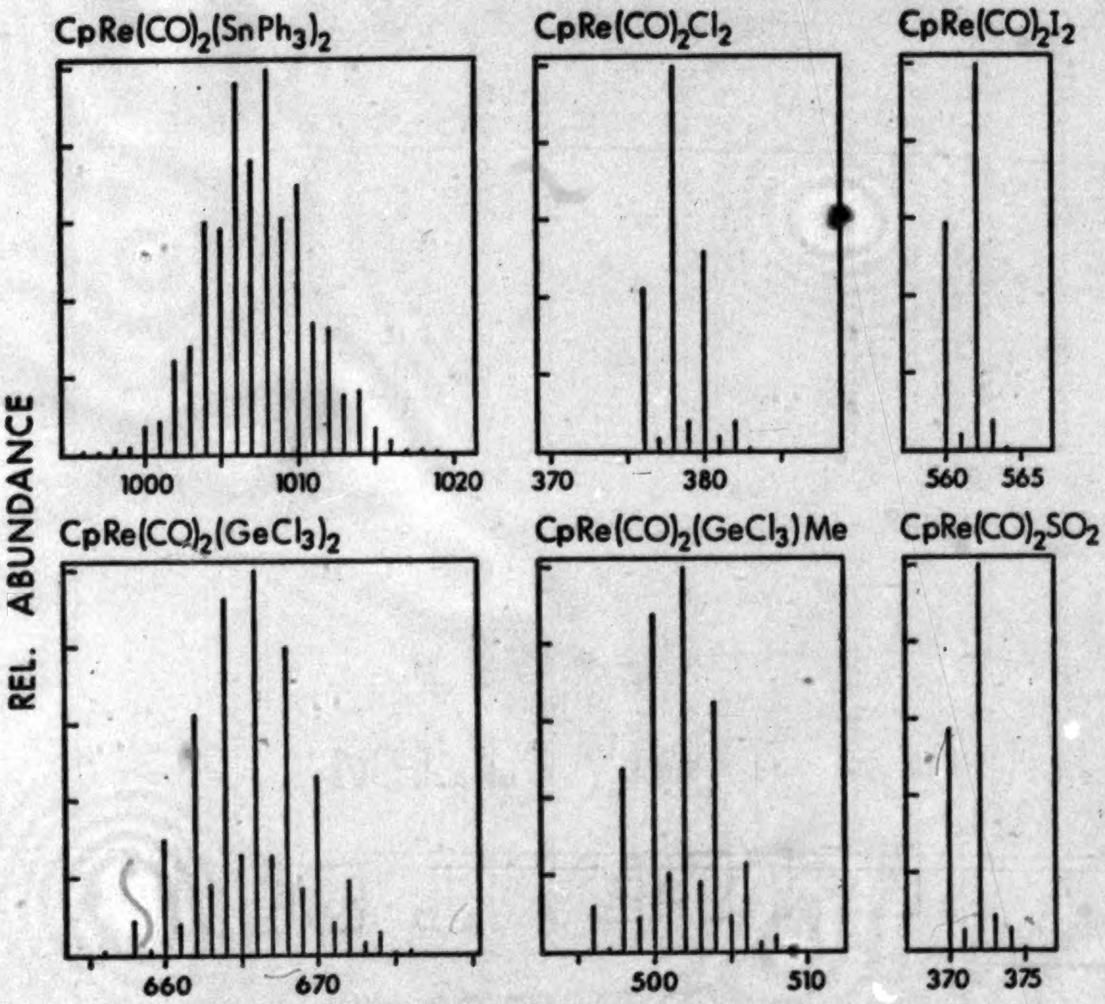
Figure 13

are uniformly at higher energy than those of bis(triphenyl-group IV) derivatives (Table VII); this observation reflects electronic effects, and possibly steric effects as well.

The manganese-hydrogen stretching frequency for *cis*-CpMn(CO)$_2$(GePh$_3$)H was not observed in solution infrared spectra, but a solid state Raman spectrum exhibited three bands in the region between 2200 cm^{-1} and 1800 cm^{-1}. Conclusive assignment of one of these bands to ν(Mn-H) cannot be made until a spectrum of the corresponding deuteride, presently unsynthesized, is recorded. Solution Raman spectra were not obtained because of the formation of bubbles, probably due to CO evolution, when the sample was placed in the laser beam. A discussion of rhenium-hydrogen stretching vibrations will be given in Part B.

The mass spectra of all the rhenium derivatives as well as *cis*-$CpMn(CO)_2(GePh_3)H$ and *trans*-$CpMn(CO)_2(GeCl_3)_2$ exhibit the expected isotope patterns for the molecular ions (e.g. Fig. 14). In each case the parent ion successively loses two carbonyl ligands before any other fragmentation occurs.

For *trans*-$CpMn(CO)_2(SnCl_3)_2$ the ion of highest nominal mass with the source temperature varying from room temperature to 230° was $C_5H_5SnCl_3^+$ (m/e 290, recorded at 110°). Other strong peaks could be assigned to the ions $C_5H_5SnCl_2^+$, $SnCl_3^+$, $C_5H_5Sn^+$, $SnCl^+$, $(C_5H_5)_2^+$, and $C_5H_5Cl^+$. No manganese- or carbonyl-containing species were seen with source temperatures of 100° or 170°. Since the closely related compounds *trans*-$CpRe(CO)_2(SnCl_3)_2$ and *trans*-$CpMn(CO)_2(GeCl_3)_2$ exhibit the expected patterns in the mass spectrometer, this behavior is certainly anomalous. Other properties of this compound offer no hint for an explanation of this behavior.



Calculated Mass Spectral Isotope Patterns

(Observed patterns closely corresponded to

calculated patterns in all cases)

Figure 14

The heaviest assignable ion for the compound *trans*-$CpMn(CO)_2(GePh_3)_2$ (source temperature 90-220°, recorded at 170°) was $Ge_2Ph_6^+$ (m/e 608). The manganese-containing ions of highest assignable mass were $CpMnGePh_3^+$ and $CpMn(CO)_2GePh_2^+$ (m/e 424 and 404, respectively). Above the ion at m/e 608, a continuous spectrum of weak peaks at every mass up to approximately 900 suggests the formation of high molecular weight species during pyrolysis of this compound. This observation seems to have no rationale when one takes into account spectra of close analogues. In this case, one would compare the mass spectrum of *trans*-$CpRe(CO)_2(SnPh_3)_2$, measured at a source temperature of 230°, in which all major peaks can be assigned from expected fragmentation of the molecular ion.

B. Preparation, Protonation, and Deuteration of Anions Derived from Et_4NEX_3 (X = Cl, Br)

1. Formation of rhenium-germanium and rhenium-tin anions

Since the preparation of rhenium and manganese hydrides from trichlorogermane was not possible using the oxidative elimination method a different synthetic route was attempted. In a series of papers, Ruff[101,173] described the use of $GeCl_3^-$ and $SnCl_3^-$ as nucleophiles in reactions with transition metal carbonyl compounds to form metal-metal bonds. Recently, $GeCl_3^-$ and $SnCl_nBr_{3-n}^-$

(n = 0, 1, 2, 3) have been used for the synthesis of mono- tris- and hexakis-(group IV trihalide) derivatives of chromium, molybdenum, and tungsten, e.g.,

$$(C_6H_6)_2Cr + 6SnBr_{3-n}Cl_n^- \rightarrow [Cr(SnBr_{3-n}Cl_n)_6]^{-6} + 2C_6H_6 \quad ^{189} \quad \text{(III-9)}$$

$$C_6H_6W(CO)_3 + 3SnCl_3^- \rightarrow [W(CO)_3(SnCl_3)_3]^{-3} + C_6H_6 \quad ^{50} \quad \text{(III-10)}$$

Since the protonation of metal anionic complexes is often a good method for obtaining metal hydride derivatives,[190] some group IV halide anions were synthesized and reacted with $CpM(CO)_3$. The anions $[CpMn(CO)_2ECl_3]^-$ were prepared by a variation of Ruff's method.[173] The $CpRe(CO)_3$ derivatives of $GeCl_3^-$, $GeBr_3^-$, and $SnCl_3^-$ were prepared by irradiation of a refluxing THF solution of $CpRe(CO)_3$ with the tetraethylammonium salts of the group IV trihalides:

$$CpRe(CO)_3 + Et_4NEX_3 \rightarrow [Et_4N][CpRe(CO)_2EX_3] + CO \quad \text{(III-11)}$$

(E = Ge, X = Cl, Br; E = Sn, X = Cl)

Although Ruff states that the $GeCl_3^-$ and $SnCl_3^-$ anions are not stable in THF, yields varying from 45-65 percent of the rhenium-group IV anions were obtained in refluxing THF following reactions times of 16-24 hours. The ionic products could best be recrystallized from dichloromethane-methanol solutions at -20°. The two carbonyl stretching bands in the infrared spectra of the anions (Table VIII) are shifted to low energy, compared to the corresponding hydrides (*vide infra*). This is typical of negatively-charged species, and reflects the delocalization of the negative charge into the antibonding orbitals of the carbonyl ligands (cf. Fig. 15 and 16).

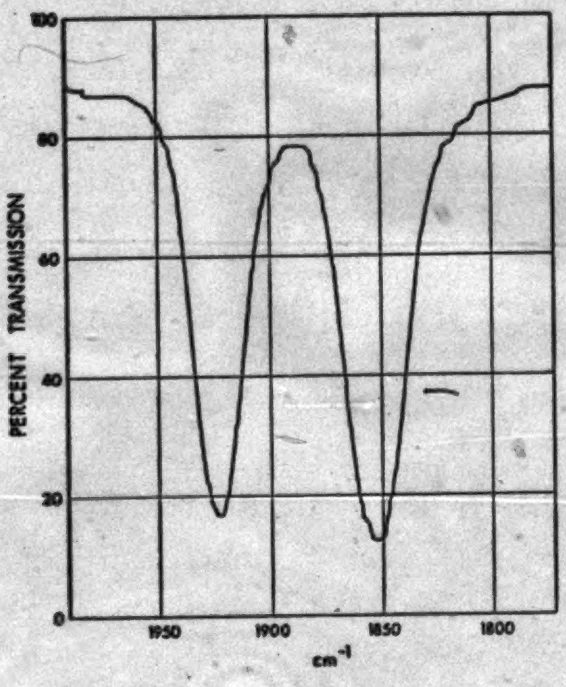
2. Formation of hydrides and deuterides

Protonation of the three rhenium-group IV anions in a rapidly stirred mixture of phosphoric acid and dichloromethane (which are immiscible) afforded good yields of the corresponding hydrides:

$$[\mathrm{CpRe(CO)_2EX_3}]^- + \mathrm{H_3PO_4} \rightarrow \textit{trans}\text{-}\mathrm{CpRe(CO)_2(EX_3)H} + \mathrm{H_2PO_4}^- \qquad \text{(III-12)}$$

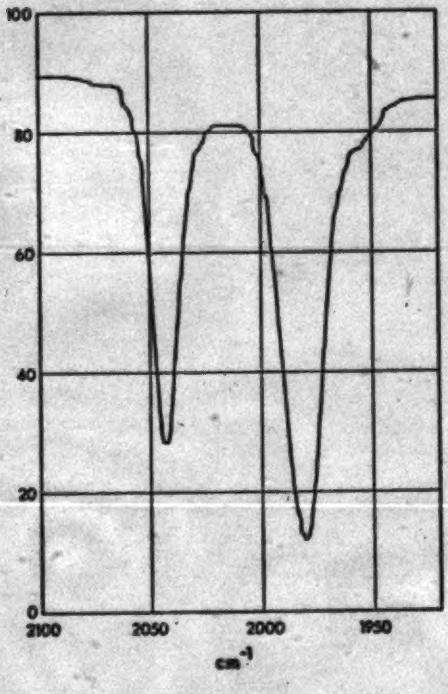
Crystallization of the hydrides sometimes proved difficult, especially when solvent removal was required from dilute solutions. The best procedure consisted of starting with a very concentrated solution of the rhenium anion in dichloromethane. After protonation and subsequent cooling to -78°, removal of the dichloromethane solution from the solid phosphoric acid and slow addition of heptane at -78° usually resulted in crystal formation after a few hours. The deuterides, *trans*-$\mathrm{CpRe(CO)_2(GeX_3)D}$, were formed in the same way from D_3PO_4. The solids are reasonably stable in air, but solutions decompose in air within an hour.

The protonation of $[\mathrm{CpMn(CO)_2ECl_3}]^-$ led to formation of the *cis* hydrides, as identified by their bands in



[Et_4N][$CpRe(CO)_2GeCl_3$]

Figure 15



trans-$CpRe(CO)_2(GeCl_3)H$

Figure 16

infrared spectra of the reaction mixtures, but solid products were not obtained on attempted crystallizations. Oils, obtained on removal of solvent, and sublimates, obtained from these oils, both showed impurities of $CpMn(CO)_3$ and other unknown products in their infrared spectra. Mass spectra of the crude products showed no molecular ion, but, in the case of the germanium derivative, mainly $CpMn(CO)_2GeCl_2^+$ and $CpMn(CO)_3^+$. The former ion would be formed from the presumed molecular ion by loss of HCl, whose presence was apparent from a large peak at m/e 36 for $H^{35}Cl$. The lack of crystallizable products thus could be rationalized by the thermal instability of *cis*-$CpMn(CO)_2(ECl_3)H$ due to facile elimination of HCl. There was no evidence for dimerization after the loss of HCl from two molecules of hydride. Because of the proximity of the hydrogen and chlorine atoms in a structure such as 25a (where X = H and Y = $GeCl_3$) the loss of HCl can probably occur with little rearrangement.

For the rhenium hydrides, *trans*-$CpRe(CO)_2(EX_3)H$, peaks in the mass spectra due to loss of hydrogen halide from the molecular ion are very intense (e.g. Table IX). For all three cases the molecular ion is much weaker than the most intense peak, and source temperatures equal to (for $CpRe(CO)_2(GeCl_3)H$) or greater than (for $CpRe(CO)_2(SnCl_3)H$ and $CpRe(CO)_2(GeBr_3)H$) the melting or decomposition points were required to record spectra exhibiting molecular ions. Consecutive loss of two carbonyl ligands from the parent minus HX peak occurred before further fragmentation of the group IV ligand. In all three spectra very weak peaks occur at masses higher than the molecular ion (especially for *trans*-$CpRe(CO)_2$-$(SnCl_3)H$, recorded at a source temperature 35° above the decomposition point). Although in some instances such peaks might lead one to suspect an incorrect assignment of the molecular ion, the molecular formulations are believed to be correct in these cases, both because of the possible thermal rearrangements in the mass spectrometer at these temperatures, and because of the other supporting spectroscopic and analytical data.

The new rhenium hydrides react in a similar fashion to the analogous silyl manganese and rhenium hydrides under substitution with triphenylphosphine[171] (as in III-1) and deprotonation with Et_3N (III-13).[171,188] The latter reaction proceeds smoothly with excess base, while with

$$trans\text{-}CpRe(CO)_2(EX_3)H + Et_3N \rightleftarrows [Et_3NH][CpRe(CO)_2EX_3] \quad \text{(III-13)}$$

an approximately equimolar amount, an equilibrium between protonated and unprotonated metal complexes is established, as indicated by bands for both species in infrared spectra. This type of equilibrium was also exhibited by the *cis*-$CpMn(CO)_2(SiCl_3)H/Et_3N$ system.[188]

3. Infrared, Raman, and nmr spectra of the hydrides and deuterides

The infrared spectra of the three rhenium anions and their corresponding hydrides and deuterides in the carbonyl region show little variation in their band frequencies (Table VIII), with the largest change being four wavenumbers. The three rhenium hydrides all show very similar proton nmr spectra. The high field proton appears at a characteristic chemical shift of c. 19.4 τ.

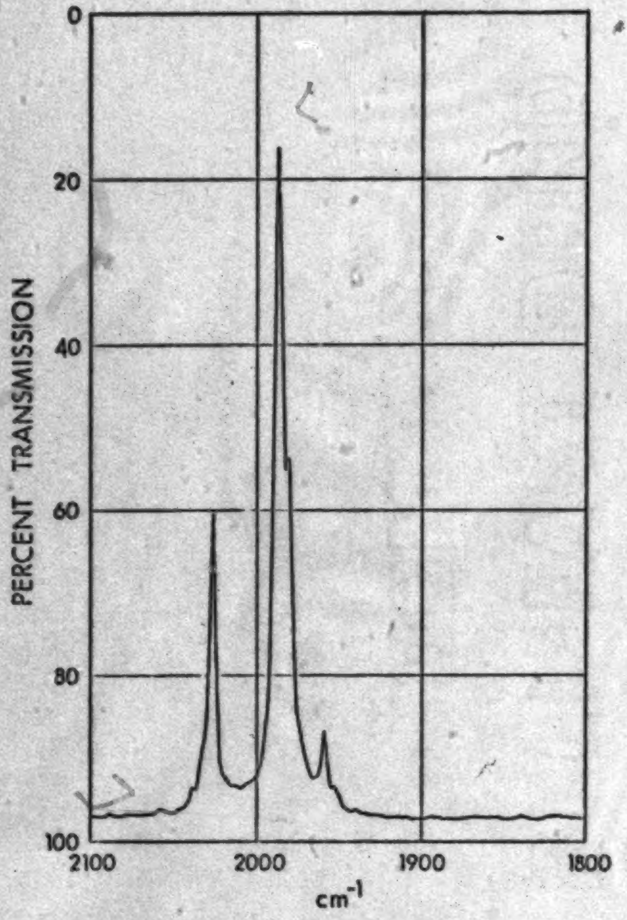
No bands assignable to rhenium-hydrogen stretching modes could be seen in the solution infrared spectra of the hydrides (see e.g. Fig. 16). This parallels the absence of such bands in infrared spectra of *cis*-$CpM(CO)_2$-

$(SiR_3)H$ compounds (R = Ph, CH_2Ph, Cl).[171] A metal-hydride stretching band is observed in the infrared only for *cis*-$CpMn(CO)_2(SiCl_3)H$[41] and *cis*-$CpMn(CO)_2(SiPhCl_2)H$.[191]

The Raman spectra of crystalline samples of *trans*-$CpRe(CO)_2(EX_3)H$ exhibited three bands in the carbonyl region (Table X, Fig. 17). One of these bands was absent in the spectra of the corresponding deuterides (Fig. 18) and a new band appeared in the region expected for a rhenium-deuterium stretching mode (Table X). Therefore the rhenium-hydrogen stretching frequencies in the carbonyl region can be assigned unambiguously. The ratios of frequencies ν(Re-H)/ν(Re-D) are 1.40, identical to the theoretical value.[192]

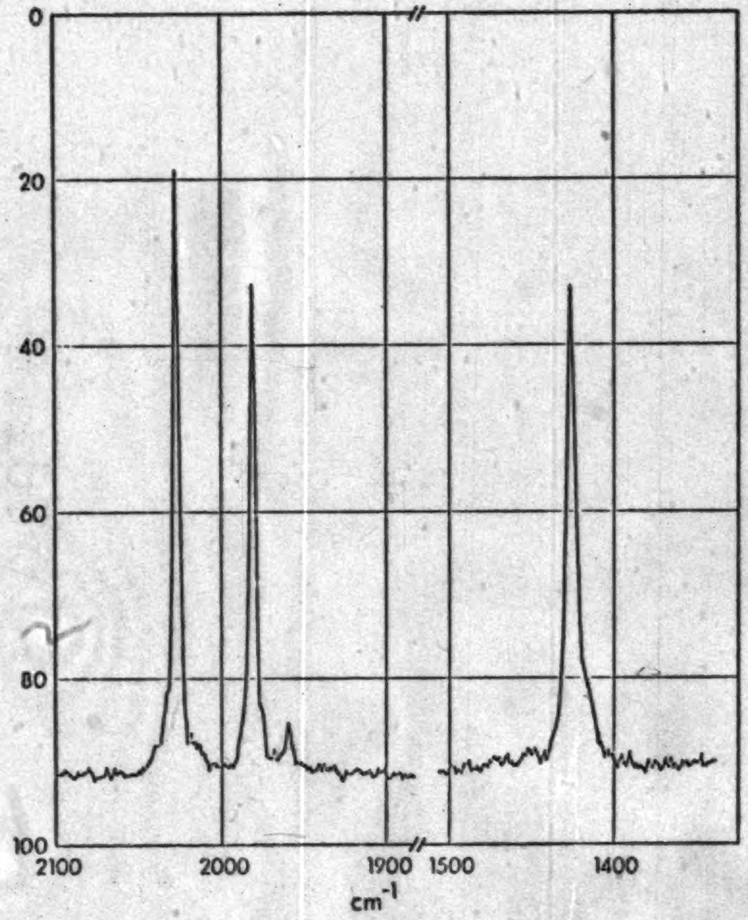
4. Synthesis of $C_6H_6Mn(CO)_2GeCl_3$

In order to extend the series of compounds containing manganese- and rhenium-group IV bonds, reactions of $[Et_4N][GeX_3]$ (X = Cl, Br) or $Li[GePh_3]$ with $[C_6H_6M(CO)_3][PF_6]$ were carried out. The group IV anions have a number of possible positions of attack on the transition metal cation. Attack on the organic ring would produce a cyclohexadienyl complex; attack at a carbonyl group would lead to an acyl type complex; and attack at the transition metal would produce a compound containing a metal-metal bond. Using various inorganic and organic nucleophiles, all three modes of attack have recently been investigated.[61,193]



trans-CpRe$(CO)_2(GeCl_3)$H

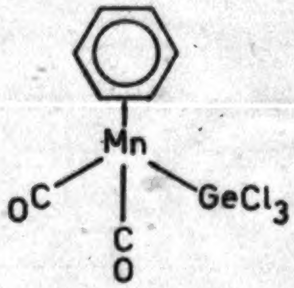
Figure 17



trans-CpRe$(CO)_2(GeCl_3)$D

Figure 18

In reactions of the $[C_6H_6Mn(CO)_3]^+$ cation with $[GeCl_3]^-$, $[GeBr_3]^-$, and $[GePh_3]^-$, infrared and mass spectral evidence suggested the existence of complexes containing manganese-germanium bonds. Only in the case of $C_6H_6Mn(CO)_2GeCl_3$, however, were reasonable microanalytical results obtained. This complex would be expected to have a structure as in 28, which is similar to some



28

$CpFe(CO)_2ER_3$ (E = Si, Sn; R = halogen or organic group) complexes, on which a great deal of infrared spectroscopic studies have recently been carried out.[171,194] Because of the similarity between 28 and the iron analogues, it was expected that further studies in these and other group IV-manganese derivatives would be of interest. Unfortunately, the reactions of the group IV anions with $[C_6H_6Re(CO)_3][PF_6]$ did not lead to any readily identifiable products.

C. Reaction of Alkylhalosulphonates with $[Et_4N][CpM(CO)_2EX_3]$ (X = Cl, Br)

1. Reactions with methyl fluorosulphonate

Methyl fluorosulphonate is known to be an effective alkylating agent[195-197] (usually more reactive than trialkyloxonium salts[198]) in transition metal chemistry. Since Et_3OBF_4 and Me_3OPF_6 failed to produce alkylated products of $[CpRe(CO)_2GeCl_3]^-$ in reasonable yield or sufficient purity for full characterization, $MeOSO_2F$ was used to obtain the desired methyl derivative. Stirring the two reactants in toluene for eight hours gave the expected product:

$$[CpRe(CO)_2GeCl_3]^- + MeOSO_2F \xrightarrow{\text{toluene}} \textit{trans}\text{-}CpRe(CO)_2(GeCl_3)Me + OSO_2F^- \quad \text{(III-14)}$$

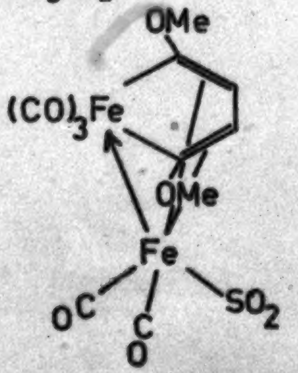
The infrared spectrum of the methyl derivative exhibited a high energy (symmetric) CO stretching band weaker than the low energy (antisymmetric) band, indicating a *trans* structure. The mass spectrum showed the molecular ion and fragmentation pattern for the compound as formulated.

The reaction between the rhenium anion and $MeOSO_2F$ in dichloromethane gave two compounds in about equal amounts. One of the compounds was identified as the expected methyl derivative, and the other was obtained as the predominant product when the reaction was carried out in acetone. This second compound proved to be the unexpected derivative, $CpRe(CO)_2SO_2$, obtained in widely variable yields:

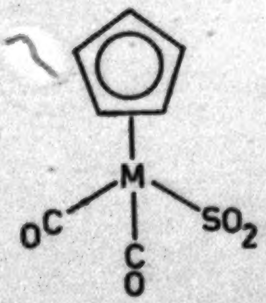
$$[CpRe(CO)_2GeCl_3]^- + MeOSO_2F \xrightarrow{\text{acetone}} CpRe(CO)_2SO_2$$
$$+ \textit{trans}\text{-}CpRe(CO)_2(GeCl_3)Me + \ldots. \qquad \text{(III-15)}$$

Although $MeOSO_2F$ is known to undergo a variety of different types of reaction,[198] this is the first time a product has been isolated that incorporates an SO_2 fragment from $MeOSO_2F$. Indeed, transition metal sulphur dioxide complexes are invariably prepared from the reaction of liquid or gaseous sulphur dioxide with a transition metal compound.

The first transition metal sulphur dioxide complexes were the ruthenium-ammine derivatives $[Ru(NH_3)_4SO_2X]X$ and $[Ru(NH_3)_5SO_2]X_2$ (X = Cl, Br), synthesized in 1936.[199] The next sulphur dioxide complex, 29, was not reported until 1963.[200] Later, other transition metal sulphur dioxide complexes were isolated, including $CpMn(CO)_2SO_2$,[201] 30a, $M(CO)_5SO_2$ (M = Cr, W),[202] a large variety of rhodium



29



30a M = Mn

30b M = Re

and iridium compounds,[203-205] and a few derivatives of palladium,[205] platinum,[205] iron,[206] ruthenium,[207] and osmium.[208] The complex isolated in this work, 30b, is the first sulphur dioxide complex of rhenium.

Single crystal X-ray analysis of a number of complexes have shown that bonding between the transition metal and the sulphur dioxide molecule can occur in two ways. In $[RuCl(NH_3)_4SO_2]^+$,[209] $Pt(SO_2)(PPh_3)_3$,[210] and $CpMn(CO)_2SO_2$,[211] the angles between the M-S bond and the normal to the SO_2 plane are all about 90°. On the other hand, in $MCl(SO_2)(PPh_3)_2CO$, (M = Rh, Ir), the same angle is about 30°.[212,213] The metal-sulfur bond lengths in the former case are much shorter than those in the latter. It has been proposed[212] that the SO_2 ligand exhibits an amphoteric nature. The iridium and rhodium sulphur dioxide complexes occur through a metal to sulphur electron pair donation with SO_2 acting as a Lewis acid; in the other cases SO_2 acts as a Lewis base, with metal back-donation to an empty ligand orbital, resulting in a shorter metal-sulphur bond and a planar $M-SO_2$ arrangement.

The rhenium complex, 30b, would presumably have a structure analogous to that of $CpMn(CO)_2SO_2$, with sulphur dioxide acting as an electron pair donor in both cases. The infrared spectrum in solution exhibits two bands each in the carbonyl region and in the S=O region, corresponding to symmetric and antisymmetric stretches of both types of functional group (Table VII). The positions of the bands compare well with those of the manganese analogue.[201] The mass spectrum exhibits the expected molecular ion isotope pattern (Fig. 14) and fragmentation, with carbonyl loss after loss of SO_2 from the parent ion.

The mechanism of formation of $CpRe(CO)_2SO_2$ still remains a mystery in spite of experiments to clarify the situation. In a separate experiment reaction III-15 was carried out in an evacuated sealed tube, and after three hours all volatiles were distilled into a mass spectrometer gas inlet tube. Analysis of the gases showed mainly Me_2CO^+ and SiF_4^+ and SiF_3^+. The presence of SiF_4 can be explained from a reaction sequence beginning with traces of water in the acetone reacting with $MeOSO_2F$:

$$\begin{tikzcd}
MeOSO_2F + H_2O \arrow[r] & HSO_3F \arrow[d, "H_2O"] + MeOH & \\
 & H_2SO_4 + HF \arrow[d, "\text{Pyrex glass}"] & \\
 & SiF_4 & \text{(III-16)}
\end{tikzcd}$$

No trace of any germanium-containing compound volatile at room temperature was seen. The red-black oily residue after the volatiles were removed was placed on a mass spectrometer direct probe with the source heated to 150°. The resulting mass spectrum showed predominantly $CpRe(CO)_2$-SO_2, with some $CpRe(CO)_2(GeCl_3)Me$ also evident. Almost all other peaks seen in the spectrum could be assigned to species from a reasonable fragmentation pattern from either $CpRe(CO)_2SO_2$ or $CpRe(CO)_2(GeCl_3)Me$. Since no unassigned peaks contained a germanium isotope pattern, the fate of the $GeCl_3$ group lost during the formation of 30b is not known.

The fact that only the methyl derivative is obtained from the reaction in toluene suggests that either the polarity of dichloromethane and acetone, or the fact that these solvents contain electronegative chlorine or oxygen atoms plays a part in the mechanism. In fact, $MeOSO_2F$ reacts with pure acetone, probably to methylate the oxygen atom initially, but decomposition to the red-black oil soon sets in.

No reaction occurred with $[Et_4N][CpRe(CO)_2GeCl_3]$ when sulphur dioxide was bubbled through a dichloromethane or acetone solution of the anion. There was also no reaction when sulphur dioxide was bubbled through dichloromethane solutions of $CpRe(CO)_2(GeCl_3)Me$ or $CpRe(CO)_2(GeCl_3)H$. Since fluosulphonic acid is possibly present in the reaction mixture via reaction III-16, the reaction of HSO_3F and $[Et_4N][CpRe(CO)_2GeCl_3]$ was carried out in dichloromethane; no heptane soluble products, and therefore no $CpRe(CO)_2SO_2$, were isolated from the reaction mixture. Under the same conditions as with $[Et_4N][CpRe(CO)_2GeCl_3]$, $[Et_4N][CpRe(CO)_2SnCl_3]$ was reacted with $MeOSO_2F$, to afford only traces of the complex, 30b. In the reaction of $\mathrm{MeOSO_2F}$ with $\mathrm{[Et_4N]}$-$\mathrm{[CpMn(CO)_2GeCl_3]}$ in acetone, traces of 30a, $\mathrm{CpMn(CO)_2SO_2}$, were detected.

2. Reactions with other alkylhalosulphonates

In order to shed some light on the processes occurring in III-15, $\mathrm{[Et_4N][CpRe(CO)_2GeCl_3]}$ was reacted with the closely related halosulphonates, $\mathrm{EtOSO_2F}$, $\mathrm{MeOSO_2Cl}$, and *n*-$\mathrm{C_4H_9OSO_2Cl}$.

In toluene, little reaction occurred on stirring the rhenium anion and $\mathrm{EtOSO_2F}$ together for 20 hours; unreacted $\mathrm{[Et_4N][CpRe(CO)_2GeCl_3]}$ was the only substance isolated. In dichloromethane, the two starting materials reacted over a few hours to give as the only carbonyl-containing product, *trans*-$\mathrm{CpRe(CO)_2(GeCl_3)Et}$ in low yield. In acetone, the same ethyl derivative was obtained, and there was no evidence for the formation of $\mathrm{CpRe(CO)_2}$-$\mathrm{SO_2}$.

In reactions of $\mathrm{MeOSO_2Cl}$ and *n*-$\mathrm{C_4H_9OSO_2Cl}$ with $\mathrm{[Et_4N][CpRe(CO)_2GeCl_3]}$ at room temperature, only one product was obtained in the solvents acetone, dichloromethane, or benzene:

$$\mathrm{[CpRe(CO)_2GeCl_3]^-} + \mathrm{ROSO_2Cl} \rightarrow \underset{\textbf{31}}{trans\text{-}\mathrm{CpRe(CO)_2(GeCl_3)Cl}} + \ldots \qquad \text{(III-17)}$$

$\mathrm{R = Me,}\ n\text{-}\mathrm{C_4H_9}$

The chloride derivative, 31, obtained in moderate yield, was also formed from the rhenium anion by reaction with chlorine (*vide infra*). The facile formation of 31 seems to favor a straightforward nucleophilic attack at the chlorine atom with either $ROSO_2^-$ or some fragment of $ROSO_2^-$ as the anionic leaving group. There seems to be no previous evidence for attack at the chlorine atom in alkylchlorosulphonates,[214] and the only previous evidence for nucleophilic attack at the chlorine atom involved arylchlorosulphonates, with inorganic nucleophiles (e.g. $S_2O_3^=$, CN^-, SO_3^-, halide ions) in aqueous ethanol.[214,215] Although nucleophilic attack at the sulphur atom, with chloride ion as a leaving group, has been detected as a minor competing reaction in systems similar to those above,[216] such a mechanism would not lead to rhenium-chlorine bond formation. There was also no evidence for the formation of $CpRe(CO)_2(GeCl_3)(SO_2Cl)$, which could be a product of nucleophilic attack at sulphur. Extrusion of SO_2 from $CpRe(CO)_2(GeCl_3)(SO_2Cl)$ would lead to the observed product, but no gas was given off during the reactions, and only bands due to the product, 31, were observed in infrared spectra of the reaction mixtures.

Concerning the formation of $CpRe(CO)_2SO_2$ (III-15), it would seem that the mechanism can only be surmised. Initial reaction might involve nucleophilic attack at the sulphur atom, with some type of interaction of a $MeOSO_2F$ fragment with the trichlorogermyl group to facilitate rhenium-germanium bond cleavage. However, there is no experimental evidence to support this supposition, and until detailed investigations of the fates of the $MeOSO_2F$ fragments and the trichlorogermyl group are carried out, no mechanism for this reaction can be proposed.

Reactions of $MeOSO_2Cl$ or n-$C_4H_9OSO_2Cl$ with $[Et_4N]$-$[CpMn(CO)_2ECl_3]$ produced no isolable carbonyl-containing compounds in dichloromethane, although bands assignable to the expected chloride derivatives were seen in the infrared spectra. Under partial vacuum, rapid evolution of a gas, probably carbon monoxide, occurred in each case.

D. Other Derivatives of $CpM(CO)_3$

The rhenium anions formed in III-11 undergo a variety of metathetical reactions expected for regular carbonylate anions.[26] However, the anions seem to have a rather low nucleophilicity, since more reactive electrophiles are needed than is usual. For example, there is no reaction with methyl iodide, but the methyl derivatives can be obtained by reaction with Me_3OPF_6 or $MeOSO_2F$. Also, no reaction occurs between the anions and EtI, Me_3SnCl, $MeGeCl_3$, and CH_3COCl. With $NOPF_6$, $[Et_4N][CpRe(CO)_2GeCl_3]$ forms the already known[217] $[CpRe(CO)_2NO][PF_6]$ by displacement of the trichlorogermyl group.

Reactions with halogens in dichloromethane produced metal halide derivatives:

$$[\mathrm{CpRe(CO)_2GeCl_3}]^- + X_2 \rightarrow \textit{trans}\text{-}\mathrm{CpRe(CO)_2(GeCl_3)X} + X^- \qquad X = \mathrm{Cl, Br, I} \qquad \text{(III-18)}$$

$$[\mathrm{CpRe(CO)_2GeBr_3}]^- + \mathrm{Br_2} \rightarrow \textit{trans}\text{-}\mathrm{CpRe(CO)_2(GeBr_3)Br} + \mathrm{Br}^- \qquad \text{(III-19)}$$

$$[\mathrm{CpRe(CO)_2SnCl_3}]^- + \mathrm{I_2} \rightarrow \textit{trans}\text{-}\mathrm{CpRe(CO)_2I_2} + \ldots. \qquad \text{(III-20)}$$

The last reaction, in which a rhenium-tin bond is cleaved by iodine, is not surprising, since iodine is known to cleave ruthenium-germanium and ruthenium-tin bonds in compounds of the form $\mathrm{Ru(CO)_4(EMe_3)_2}$.[218] In the case of $\mathrm{Ru(CO)_4(GeMe_3)_2}$, only trace amounts of $\mathrm{Ru(CO)_4(GeMe_3)I}$ were found on refluxing the ruthenium complex with iodine in hexane, whereas both $\mathrm{Ru(CO)_4(SnMe_3)I}$ and *cis*-$\mathrm{Ru(CO)_4I_2}$ were obtained at -5° from the reaction of the ruthenium-tin complex and iodine. Other cases of halogen cleavage of group IV-transition metal bonds have more recently been investigated. These involve the reactions of chlorine and iodine, which result in the cleavage of Si-Fe, Ge-Fe, Sn-Fe, Sn-Cr, Sn-Mo, Sn-W, and Sn-Mn bonds.[73,219] It would seem from both the present work and the work cited above that transition metal-germanium bonds are less prone to cleavage by iodine than transition metal-tin bonds. No traces of any dihalide derivatives were obtained in reactions of halogens with the rhenium-germanium anions.

The dibromide analogue of the product of III-20, $CpRe(CO)_2Br_2$, was synthesized in 1969 by the direct action of bromine on $CpRe(CO)_3$ in the presence of trifluoroacetic acid.[220] The authors stated that under the electrophilic substitution conditions, the first step may be assumed to involve bromonium ion attack on the tricarbonyl with subsequent substitution of CO by Br^-:

$$CpRe(CO)_3 \xrightarrow{Br^+} [CpRe(Br)(CO)_3]^+ \xrightarrow{Br^-} CpRe(CO)_2Br_2 + CO \qquad \text{(III-21)}$$

The stereochemistry of $CpRe(CO)_2Br_2$ was not indicated in the 1969 publication. Both carbonyl infrared bands were designated as "very strong" in cyclohexane solution. In the present work, $CpRe(CO)_2Br_2$ was found as a minor product from the reaction of allyl bromide with $CpRe(CO)_3$ (see Chapter IV). Identified by infrared and mass spectra, the compound obtained by this method exhibited a carbonyl stretching band intensity pattern indicative of a *trans* structure in cyclohexane. The diiodide analogue also has a *trans* structure, as indicated by the band intensities in dichloromethane (Fig. 19).

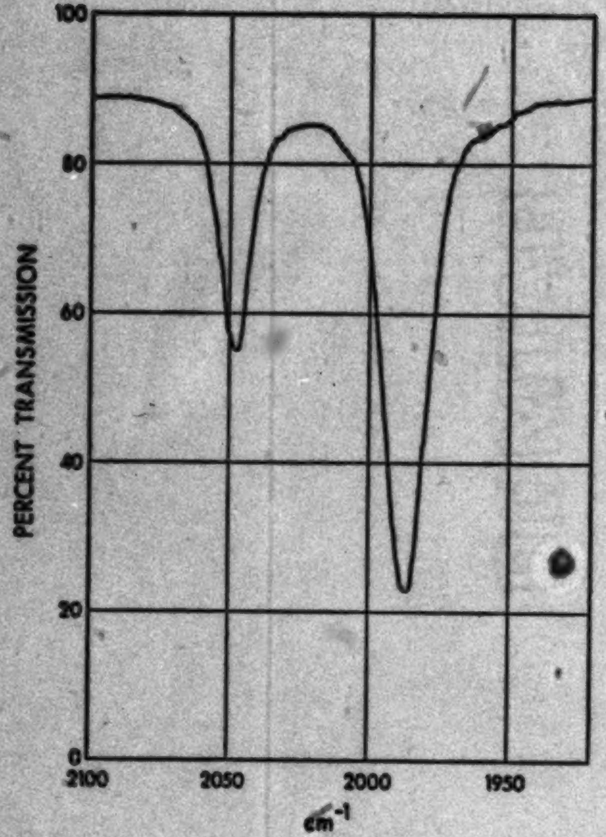
The infrared spectra of the group IV halide complexes $CpRe(CO)_2(EX_3)X$ all exhibit a band pattern in the carbonyl stretching region expected for *trans* isomers in solution (Table VII). The positions of the bands show a general trend to lower wavenumbers as the rhenium substituent varies down the group Cl to Br to I. This trend parallels that of $M(CO)_5X$ complexes, observed from force constant work,[12] and infrared band positions.[221]

The mass spectra of the $CpRe(CO)_2(EX_3)X$ complexes exhibit molecular ions, expected isotope combination patterns, and consecutive loss of two carbonyl ligands from the parent ion. Only for the tetrachloride derivatives, *trans*-$CpRe(CO)_2(ECl_3)Cl$, did loss of a halogen atom and loss of a carbonyl ligand from the molecular ion occur to approximately the same extent.

Reactions of halogens with the manganese anions $[Et_4N][CpMn(CO)_2ECl_3]$ in dichloromethane solutions afforded no carbonyl-containing compounds isolable from the reaction mixtures. Although in most cases infrared spectra of reaction mixtures indicated probable formation of the expected product, all solids obtained from these reactions were unidentifiable from infrared and mass spectra (except for traces of $CpMn(CO)_3$ and unreacted anion).

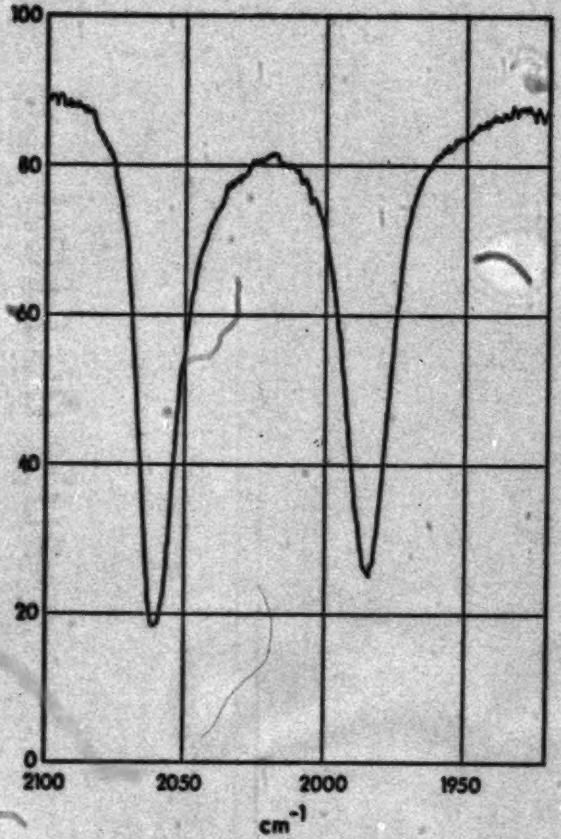
The only manganese-group IV compound isolated as a derivative of the manganese anions was *trans*-$CpMn(CO)_2(SnCl_3)_2$ from the reaction between $[Et_4N][CpMn(CO)_2SnCl_3]$ and $SnCl_4$ in dichloromethane.

Attempted recrystallization of the halide derivative *trans*-$CpRe(CO)_2(GeCl_3)Cl$ at room temperature from a dichloromethane-methanol solution led to the isolation of a methoxide product:



trans-CpRe(CO)$_2$I$_2$

Figure 19



cis-CpRe(CO)$_2$Cl$_2$

Figure 20

$$trans\text{-}CpRe(CO)_2(GeCl_3)Cl + MeOH \rightarrow HCl + trans\text{-}CpRe(CO)_2[Ge(OMe)Cl_2]Cl \quad \text{(III-22)}$$

Further reactions with both methanol and ethanol were carried out at the reflux temperature of the alcohol to ensure complete reaction.

Although infrared band positions and relative intensities for the chloride and alkoxide derivatives are very similar (Table VII), unambiguous characterization of each compound was obtained through nmr and exact mass spectral measurements, as well as microanalyses. The measured masses for the most abundant isotopes in the molecular ions of the chloride and methoxide derivatives were within 2 and 0.8 parts per million, respectively, of the calculated masses (Table VII). The nmr spectra of the methoxide and ethoxide complexes exhibited absorptions in the expected regions, and the correct integration amplitudes, within experimental error, for the presence of only one alkoxide group in each complex (Table XI).

The position of substitution of the methoxide group was determined by solid state infrared spectroscopy. In the region between 1200 and 700 cm^{-1} the spectrum of *trans*-CpRe(CO)$_2$[Ge(OMe)Cl$_2$]Cl exhibits two strong bands, at 1020 and 848 cm^{-1}, which can be assigned to the C-O and Ge-O stretching modes, respectively (Table XII).[57] These bands are absent in a similar spectrum of *trans*-CpRe(CO)$_2$(GeCl$_3$)Cl. Therefore substitution of a chlorine atom occurs at the germanium atom and the rhenium-chlorine bond remains intact.

The above reactions employing excess alcohol can be contrasted with the efficient preparation of alkoxygermanes from halogermanes by direct alcoholysis, employing a stoichiometric amount of alcohol, and a tertiary amine to remove the hydrogen halide:

$$R_{4-n}GeX_n \;+\; nR'OH \;+\; nR''_3N \;\rightarrow\; R_{4-n}Ge(OR')_n \;+\; n[R''_3NH]X^{123} \qquad (n = 1\text{-}4) \qquad \text{(III-23)}$$

Reactions of transition metal bonded chlorogermanes are also fairly common:

$$CpFe(CO)_2GeCl_3 \;+\; 3MeOH \;+\; 3NH_3 \;\rightarrow\; CpFe(CO)_2Ge(OMe)_3 \;+\; 3NH_4Cl^{109} \qquad \text{(III-24)}$$

However, in the reaction at hand, only one chloride ion is substituted, even in the presence of excess alcohol. When reaction III-22 was carried out in the presence of either ammonia or triethylamine, infrared spectra of the reaction mixtures indicated a complex reaction, from which no alkoxide derivatives could be identified.

In an attempt to synthesize $CpRe(CO)_2[Sn(OMe)Cl_2]Cl$ by reaction of $CpRe(CO)_2(SnCl_3)Cl$ with MeOH, the surprising product was *cis*-$CpRe(CO)_2Cl_2$, obtained in low yield:

$$\textit{trans}\text{-}CpRe(CO)_2(SnCl_3)Cl \;+\; MeOH \;\xrightarrow[80°]{\text{sealed tube}}\; \textit{cis}\text{-}CpRe(CO)_2Cl_2 \;+\; \ldots. \qquad \text{(III-25)}$$

Since the reaction was not always reproducible, the pathway for the formation of the dichloride is not known. One possibility might be the formation of the expected methoxide product with elimination of HCl, with subsequent cleavage of the rhenium-tin bond by the HCl.

The infrared spectrum shows two carbonyl stretching frequencies with the characteristic relative intensities for a *cis* configuration (Fig. 20), in contrast to *trans*-$CpRe(CO)_2I_2$ (Fig. 19). Both $CpRe(CO)_2$-dihalides synthesized in this work exhibit molecular ions in the mass spectra, as well as the expected isotope combinations (Fig. 14) and fragmentation patterns. This evidence, together with the analytical data, confirms their formation by these unorthodox methods.

E. Summary

The transition metal-group IV hydrides prepared in this work differ from the transition metal-silicon hydride analogues mainly in their isomeric structures. The bonding interaction between the hydrogen and silicon atoms in the latter compounds, which are *cis* structures, would be virtually impossible in the *trans* structures of the rhenium hydrides of germanium and tin. (An X-ray crystallographic study of *trans*-$CpRe(CO)_2(GeCl_3)H$ currently in progress should eventually support this contention.) On the other hand, it would be of great interest to determine the structure of *cis*-$CpMn(CO)_2(GePh_3)H$, and in particular to determine the position of the hydride ligand with respect to the germanium atom. A kinetic study of the reductive elimination of Ph_3GeH from *cis*-$CpMn(CO)_2(GePh_3)H$ with triphenylphosphine would also be of interest to compare with the reactions of the silyl analogues.

The synthesis of the new manganese- and rhenium-group IV derivatives in this work has significantly increased the number of such known compounds, and concurrently increased the knowledge of their chemistry. Certain anomalous reactions, including those of Cl_3GeH with $CpRe(CO)_3$ and $[Et_4N][CpRe(CO)_2GeCl_3]$ with $MeOSO_2F$ have opened areas for further research in order to elucidate the mechanisms involved.

TABLE VII

INFRARED CARBONYL STRETCHING FREQUENCIES FOR DERIVATIVES OF $CpMn(CO)_3$ AND $CpRe(CO)_3$ AND MISCELLANEOUS COMPOUNDS

Compound[a]	Stretching Frequencies,[b] cm^{-1}			
	In dichloromethane		In heptane	
$CpMn(CO)_2(GeCl_3)_2$	2036(m)	1994(s)	2039(m)	2001(s)
$CpMn(CO)_2(SnCl_3)_2$	2020(m)	1981(s)		
$CpRe(CO)_2(GeCl_3)_2$	2050(m)	1996(s)	2052(m)	2004(s)
$CpRe(CO)_2(SnCl_3)_2$[c]	2038(m)	1991(s)		
$CpMn(CO)_2(GePh_3)_2$	1955(m)	1900(s)		
$CpRe(CO)_2(SnPh_3)_2$	1954(m)	1897(s)		
$CpRe(CO)_2(GeCl_2Et)_2$[c]	2078(m)	2011(s)		
$CpRe(CO)_2(GeCl_3)Cl$[d]	2066(m)	2006(s)	2066(w)	2011(m)[e]
$CpRe(CO)_2(GeCl_3)Br$	2061(m)	2004(s)	2063(w)	2010(m)[e]
$CpRe(CO)_2(GeCl_3)I$	2049(m)	1993(s)	2053(w)	2003(m)[e]
$CpRe(CO)_2(SnCl_3)Cl$	2064(m)	2009(s)		
$CpRe(CO)_2(GeBr_3)Br$	2059(m)	2001(s)		
$CpRe(CO)_2(GeCl_3)Me$[f]	2034(m)	1971(s)		
$CpRe(CO)_2(GeCl_3)Et$[c]	2042(m)	1981(s)		
$CpRe(CO)_2[Ge(OMe)Cl_2]Cl$[g]	2065(m)	2006(s)	2069(w)	2016(m)[e]
$CpRe(CO)_2[Ge(OEt)Cl_2]Cl$	2066(s)	2008(vs)	2066(s)	2012(vs)
$CpRe(CO)_2(GePh_3)Me$[c]	1996(m)	1934(s)		
$CpRe(CO)_2SO_2$[h]	2021(s)	1958(vs)	2021(s)	1965(vs)
$CpRe(CO)_2Cl_2$	2060(vs)	1984(s)		
$CpRe(CO)_2I_2$	2048(m)	1987(s)		

TABLE VII (continued)

Compound[a]	Stretching Frequencies,[b] cm^{-1}	
	In dichloromethane	In heptane
$C_6H_6Mn(CO)_2GeCl_3$	2007(vs) 1966(s)	
$C_6H_6Cr(CO)_2(GeCl_3)_2$	2006(m) 1961(s)	

[a] All *trans* isomers except $CpRe(CO)_2SO_2$, $C_6H_6Mn(CO)_2GeCl_3$, and *cis*-$CpRe(CO)_2Cl_2$.

[b] Abbreviations as in Table II.

[c] Characterized by infrared and mass spectrometry only.

[d] Exact mass calculated, 523.7771; observed, 523.7783.

[e] In saturated solutions.

[f] Exact mass calculated, 501.8336; observed, 501.8346.

[g] Exact mass calculated, 517.8285; observed, 517.8289.

[h] In C_6H_6, $\nu(S{=}O)$ 1285(m), 1108(s); as solid in KBr disc, $\nu(S{=}O)$ 1279(m), 1100(s).

TABLE VIII

INFRARED CARBONYL STRETCHING FREQUENCIES AND PROTON NMR DATA FOR METAL ANIONS AND HYDRIDES

Compound	Stretching Frequencies,[a] cm^{-1}		Chemical Shifts,[b] (τ)		
			Cp	M-H	Solvent
$[Et_4N][CpRe(CO)_2GeCl_3]$	1923(s)	1852(s)			
$[Et_4N][CpRe(CO)_2GeBr_3]$	1924(s)	1855(s)			
$[Et_4N][CpRe(CO)_2SnCl_3]$	1923(s)	1856(s)			
$[Et_4N][C_6H_6Cr(CO)_2GeCl_3]$	1893(s)	1835(m-s)			
$[Et_4N][C_6H_6Cr(CO)_2SnCl_3]$	1895(s)	1838(m-s)			
trans-$CpRe(CO)_2(GeCl_3)H$[c]	2043(m)	1981(s)	4.42	19.39	CD_2Cl_2
trans-$CpRe(CO)_2(GeBr_3)H$	2041(m)	1980(s)	4.46	19.18	$CDCl_3$
trans-$CpRe(CO)_2(SnCl_3)H$	2040(m)	1981(s)	4.37	19.29	CD_2Cl_2
cis-$CpMn(CO)_2(GePh_3)H$[d]	1981(vs)	1920(s)	4.00	19.25	C_6D_6

[a] In CH_2Cl_2, abbreviations as in Table II.

[b] All singlets, relative to TMS; peak integrals were consistent with the formulations.

[c] In heptane, 2046(w), 1990(m).

[d] In heptane, 1988(vs), 1933(s).

TABLE IX

MASS SPECTRUM OF *trans*-$CpRe(CO)_2(GeBr_3)H$[a]

m/e[b,c]	Relative Abundance[d]	Probable ion[e]
622	2.2	$C_5H_5Re(CO)_2(GeBr_3)H^+$
565	0.9	$C_5H_5ReGeBr_3^+$
540	50.9	$C_5H_5Re(CO)_2GeBr_2^+$
512	41.8	$C_5H_5Re(CO)GeBr_2^+$
484	49.9	$C_5H_5ReGeBr_2^+$
461	9.3	$C_5H_5Re(CO)_2GeBr^+$
433	6.9	$C_5H_5Re(CO)GeBr^+$
405	43.9	$C_5H_5ReGeBr^+$, $Re(CO)_2Br^+$
388	34.6	$C_5H_5Re(CO)_2HBr^+$
377	26.2	$Re(CO)Br_2^+$
360	25.6	$C_5H_5Re(CO)HBr^+$
331	100.0	$C_5H_5ReBr^+$
322	13.1	$Re(CO)_2Br^+$
308	38.9	$C_5H_5Re(CO)_2^+$
294	14.9	$Re(CO)Br^+$
280	68.1	$C_5H_5ReCO^+$
271	18.1	$Re(CO)_3^+$
252	40.3	$C_5H_5Re^+$
250	42.5	$C_5H_3Re^+$, $C_5H_5{}^{185}Re^+$
224	54.9	ReC_3H^+
200	21.4	$ReCH^+$
187	15.8	Re^+
153	79.9	$GeBr^+$

TABLE IX (continued)

$m/e^{b,c}$	Relative Abundance[d]	Probable ion[e]
80	78.9	HBr^+
28	6.5	CO^+

[a] Source temperature 150°.

[b] Most intense peaks of isotope patterns.

[c] Peaks of nominal mass higher than 622 had relative abundances << 1.0.

[d] The most intense peak in the spectrum is assigned the value 100.0.

[e] Assignments based on ^{187}Re, ^{74}Ge, ^{79}Br, $^{79}Br_2$, or $^{79}Br_2{}^{81}Br$.

TABLE X

RAMAN STRETCHING FREQUENCIES FOR MANGANESE AND RHENIUM HYDRIDES AND DEUTERIDES[a,b]

Compound	Phase	ν(C≡O)		ν(M-H)	ν(M-D)
cis-$CpMn(CO)_2(GePh_3)H$[c]	solid	1967(s)	1912(s)	1907(m-s)	
trans-$CpRe(CO)_2(GeCl_3)H$	CH_2Br_2 solution	2044(m)	1982(s)		
trans-$CpRe(CO)_2(GeCl_3)H$	solid	2027(m)	1981(m)	1987(s)	
trans-$CpRe(CO)_2(GeCl_3)D$	solid	2027(vs)	1981(s)		1426(s)
trans-$CpRe(CO)_2(GeBr_3)H$	solid	2024(s)	1978(vs)	1981(vs)	
trans-$CpRe(CO)_2(GeBr_3)D$	solid	2023(s)	1977(m-s)		1421(m)
trans-$CpRe(CO)_2(SnCl_3)H$	solid	2023(s)	1978(s)	1990(m)	

[a] In cm^{-1}.

[b] Abbreviations as in Table II.

[c] The assignment of the bands at 1912 and 1907 cm^{-1} may be reversed.

TABLE XI

PROTON NMR DATA FOR DERIVATIVES OF $CpRe(CO)_3$[a,b]

Compound	Chemical Shifts, τ[c,d]		
	Cp	Me	CH_2
trans-$CpRe(CO)_2(GeCl_3)Me$	4.46	8.85	
trans-$CpRe(CO)_2[Ge(OMe)Cl_2]Cl$	4.16	6.28	
trans-$CpRe(CO)_2[Ge(OEt)Cl_2]Cl$	4.14	8.75 (triplet)	5.97 (quartet)
$CpRe(CO)_2SO_2$	4.30		

[a] In CD_2Cl_2.

[b] Integrations of all absorptions confirmed the molecular formulations in all cases.

[c] Relative to TMS.

[d] All singlets except as noted.

TABLE XII

INFRARED STRETCHING FREQUENCIES OF SOLID *trans*-$CpRe(CO)_2[Ge(OMe)Cl_4]Cl$[a] BETWEEN 4000 AND 600 CM^{-1}

Frequency,[b] cm^{-1}	Assignment
3096(s)	C-H stretch
2960(w)	C-H "
2940(w)	C-H "
2920(m)	C-H "
2816(m)	C-H " or overtone
2050-1950(vs)	C≡O "
1625(w)	C=C "
1435(w)	C-H bend
1427(m)	C-H "
1410(m)	C-H "
1350(w)	C-H "
1020(vs)	C-O stretch
848(s)	Ge-O stretch
815(m)	C-H bend
610(m)	Re-C-O bend

[a] KBr disc.

[b] Abbreviations as in Table II.

TABLE XIII

COLOURS, MELTING POINTS, AND ANALYTICAL DATA FOR DERIVATIVES OF $CpMn(CO)_3$ AND $CpRe(CO)_3$ AND MISCELLANEOUS COMPOUNDS

Compound	Mp, °C	Colour	Calculated %			Found %		
			C	H	X[b]	C	H	X[b]
$CpMn(CO)_2(GeCl_3)_2$	dec. 160	pale yellow	15.8	0.94	39.8	16.6	1.41	37.5
$CpMn(CO)_2(SnCl_3)_2$	90-95	red-brown	13.4	0.80	34.0	13.9	1.05	33.3
$CpRe(CO)_2(GeCl_3)_2$	dec. 90	white	12.6	0.76	32.0	12.7	0.99	30.4
$CpMn(CO)_2(GePh_3)_2$	dec. 120	pale brown	65.9	4.50		66.1	4.75	
$CpRe(CO)_2(SnPh_3)_2$	240-250	pale brown	51.3	3.50		50.2	3.47	
$CpRe(CO)_2(GeCl_3)Cl$	140-144	yellow	16.1	0.97	27.2	16.4	0.93	27.0
$CpRe(CO)_2(GeCl_3)Br$	148-155	orange	14.9	0.89	32.9[c]	15.3	1.04	31.2[c]
$CpRe(CO)_2(GeCl_3)I$	136-139	orange	13.7	0.82	17.4[d]	13.9	0.91	17.3[d]
$CpRe(CO)_2(SnCl_3)Cl$	157-160	yellow	14.8	0.89	25.0	15.1	1.17	25.4
$CpRe(CO)_2(GeBr_3)Br$	155-160	red-brown	12.0	0.72	45.7	12.3	0.71	46.6
$CpRe(CO)_2(GeCl_3)Me$	163-168	pale brown	19.2	1.61	21.2	19.7	1.68	21.4
$CpRe(CO)_2[Ge(OMe)Cl_2]Cl$	107-110	yellow	18.6	1.56	20.6	18.8	1.67	21.1
$CpRe(CO)_2[Ge(OEt)Cl_2]Cl$	95-103	yellow	20.4	1.90	20.0	20.1	1.82	20.3

TABLE XIII (continued)

Compound	Mp, °C	Colour	Calculated %			Found %		
			C	H	X[b]	C	H	X[b]
$CpRe(CO)_2SO_2$ [e]	140-145	yellow	22.6	1.36	0.00	22.9	1.61	0.00
$CpRe(CO)_2Cl_2$	dec. 155	orange	22.2	1.33	18.8	22.5	1.84	19.1
$CpRe(CO)_2I_2$	dec. 120	orange-brown	15.0	0.90	45.2	14.6	1.19	44.6
$C_6H_6Mn(CO)_2GeCl_3$	175-180	yellow	26.1	1.64	28.9	26.5	1.64	28.4
$C_6H_6Cr(CO)_2(GeCl_3)_2$	dec. 160	orange	17.7	1.11	39.1	17.9	1.38	38.4

[a] All *trans* isomers except $CpRe(CO)_2SO_2$, *cis*-$CpRe(CO)_2Cl_2$, and $C_6H_6Mn(CO)_2GeCl_3$.

[b] X = Cl or Br.

[c] Total halogen content, calculated from AgX titration result, assuming Cl:Br ratio of 3:1.

[d] For Cl. Calculated for I, 20.7; found, 20.4.

[e] Calculated for S, 8.63; found, 8.04. Osmometric molecular weight in dibromomethane, calculated, 371; found, 371.

TABLE XIV

COLOURS, MELTING POINTS, AND ANALYTICAL DATA FOR METAL ANIONS AND HYDRIDES

Compound	Mp, °C	Colour	Calculated %				Found %			
			C	H	N	X^a	C	H	N	X^a
$[Et_4N][CpRe(CO)_2GeCl_3]$	144-146	yellow	29.2	4.09	2.27	17.3	29.3	4.35	2.42	17.1
$[Et_4N][CpRe(CO)_2GeBr_3]$	dec. 100	yellow	24.0	3.36	1.87	32.0	23.8	3.60	2.14	32.2
$[Et_4N][CpRe(CO)_2SnCl_3]$	124-125	pale yellow	27.2	3.80	2.11	16.1	27.1	3.90	2.32	15.8
$[Et_4N][C_6H_6Cr(CO)_2GeCl_3]$	dec. 130	red	38.8	5.29	2.83	21.5	38.7	5.27	3.14	21.6
$[Et_4N][C_6H_6Cr(CO)_2SnCl_3]$	dec. 137	red	35.5	4.84	2.59	19.6	35.2	5.29	2.31	20.0
trans-$CpRe(CO)_2(GeCl_3)H$	110-115	white	17.3	1.24		21.8	17.1	1.22		22.2
trans-$CpRe(CO)_2(GeBr_3)H$	139-145	pale brown	13.6	0.97		38.6	13.6	1.15		39.8
trans-$CpRe(CO)_2(SnCl_3)H$	dec. 125	pale yellow	15.8	1.13		19.9	15.9	1.30		20.9
cis-$CpMn(CO)_2(GePh_3)H$	86-90	pale yellow	62.4	4.40			62.2	4.58		

[a] X = Cl or Br.

EXPERIMENTAL

General Techniques and Instrumentation

A nitrogen atmosphere was maintained during all reactions and workup procedures by the use of Schlenk apparatus. Sealed tube reactions and irradiations employing the 450 watt Hanovia lamp were carried out as described in Chapter II.

Some reactions employing the 140 watt Hanovia lamp were carried out without a cooling condenser. In these cases the reaction materials were placed in a 350 ml quartz round-bottomed flask equipped with a stop-cocked side-arm, and a water-cooled reflux condenser. The solutions were allowed to reflux gently by utilizing the heat produced by the lamp during irradiation. Sometimes it was necessary to wrap the flask partially with aluminum foil to trap the heat given off during irradiation.

Small scale irradiations (≤ 100 ml solvent) were carried out using the small scale apparatus described in the previous chapter, employing either the 140 watt Hanovia lamp, or a Canadian General Electric 100 watt H38 mercury lamp. All reaction mixtures were stirred magnetically, and, except for those that were refluxed, irradiated solutions were kept about room temperature.

It should be noted here that although some synthetic procedures include much detail for the crystallization steps, crystallization was often not a certainty, and under the same conditions oils sometimes formed. In other cases only impure solids were obtained after removal of some of the solvent on a vacuum line. However, the conditions stated were found to be the best, despite sometimes giving erratic results.

Melting points, microanalyses, infrared, nmr, and mass spectra were obtained as in Chapter II, except that a Varian Model HA-100 spectrometer was used for some nmr spectra. For mass spectra, in cases where the molecular ion is not detected, and a source temperature range is given, the spectrum recorded at the stated temperature was the most complete throughout the temperature range, and no significant ions of higher nominal mass were detected at other temperatures in the range given. Raman spectra were obtained on a Spex Laser Raman spectrometer, Ramalog, using argon or krypton lasers (excitation frequencies, 6471 and 4880 Å for solid samples, 6471 and 5682 Å for solution samples).

Materials

Heptane, petroleum ether (50-80°), and dichloromethane were distilled under nitrogen, as described previously, prior to use. Methanol and ethanol were distilled from magnesium under nitrogen before use. All other solvents were of reagent grade and were saturated with nitrogen prior to use.

Chemicals were purchased as follows: dirhenium decacarbonyl from Pressure Chemical Co., Pittsburgh; benzene chromium tricarbonyl and triphenylgermane from Strem Chemicals Inc., Danvers, Mass.; stannic chloride from Fisher Scientific Co., Fair Lawn, N. J.; triphenyltin chloride from M&T Chemicals Inc., Richmond, Ca.; methyl and ethyl fluorosulphonate from Aldrich Chemical Co., Milwaukee, Wis.; germanium dioxide from The Eagle-Picher Co., Quapaw, Okla.; and cyclopentadienylmanganesetricarbonyl and trichlorogermane from Alfa Inorganics, Inc., Beverly, Mass. Florisil (100-200 mesh) and silicic acid (100 mesh) for chromatography were purchased from J. T. Baker Chemical Co., Phillipsburg, N. J. and Mallinckrodt Chemical Works, Montreal, respectively. All commercially-obtained chemicals were used as supplied unless otherwise stated.

Ethyldichlorogermane was prepared from trichlorogermane and tetraethyllead using the procedure of Mironov and Kravchenko.[222] Phenyldichlorogermane was prepared from phenylgermane and chloromethyl methyl ether following the method of Satgé and Rivière.[167] Triphenylstannane was prepared from triphenylstannyl lithium and ammonium chloride following the procedure of Allan.[223]

The tetraethylammonium salts of the trichlorogermyl and trichlorostannyl anions were prepared from the divalent metal chlorides by a method given by Parshall.[224] The analogous tribromogermyl anion was prepared by an adaptation of Parshall's method. For the *in situ* preparation of the germanium dihalide, germanium dioxide was substituted for germanium tetrachloride. By adding appropriate amounts of hypophosphorous and hydrobromic acid, and precipitating the desired compound by adding tetraethylammonium bromide, $[Et_4N][GeBr_3]$ was prepared in 72% yield.

Methyl and *n*-butyl chlorosulphonate were prepared by the method of Binkley and Degering[225] from the appropriate alcohol and sulphuryl chloride. The hexafluorophosphate salts of the benzenemanganesetricarbonyl and benzenerheniumtricarbonyl cations were prepared from the metal pentacarbonyl chlorides and benzene by the method of Winkhaus, Pratt, and Wilkinson.[226]

Procedures

Synthesis of $CpRe(CO)_3$

Samples of this compound were prepared by using a slight modification of the procedure given by Green and Wilkinson.[227] A mixture of rhenium carbonyl (10.0 g, 15.3 mmol) and dicyclopentadiene (60 g, 0.45 mol) was refluxed at 210° for 20 hours in a 500 ml round-bottomed flask that permitted a reasonable amount of foaming of the reaction mixture. After cooling the mixture to about 45°, 150 ml petroleum ether was added, and the solution was cooled to -20°. The resulting solid was recrystallized from hot heptane and then sublimed at 50° (0.02 mm) to afford white crystals of $CpRe(CO)_3$. Yields varied from 3.6 to 6.7 g (35-65%).

Synthesis of *trans*-$CpMn(CO)_2(GePh_3)_2$

A solution of $CpMn(CO)_3$ (0.50 g, 2.4 mmol) and Ph_3GeH (1.5 g, 5.0 mmol) in 50 ml heptane was irradiated with the 140 watt source at room temperature for ten hours. Infrared spectra of the reaction mixture showed only about 30% of the $CpMn(CO)_3$ had reacted after five and ten hours. The heptane solution and dichloromethane washings from the reaction vessel were combined, and the mixture was evaporated to dryness on a rotary evaporator. Unreacted Ph_3GeH and $CpMn(CO)_3$ were sublimed *in vacuo* from the residue, which was then dissolved in a small amount of dichloromethane. This oily liquid was passed through 100 g silicic acid by suction filtration. Elution with 150 ml petroleum ether removed more Ph_3GeH, $CpMn(CO)_3$, and a small amount of product. Further elution with a 150 ml mixture of 1:1 dichloromethane:petroleum ether gave a solution of the product. Evaporation to dryness and recrystallization from dichloromethane-heptane at -20° afforded about 30 mg (4%) of pure *trans*-$CpMn(CO)_2(GePh_3)_2$.

Synthesis of *cis*-$CpMn(CO)_2(GePh_3)H$

A solution of $CpMn(CO)_3$ (0.75 g, 3.7 mmol) and Ph_3GeH (1.2 g, 4.0 mmol) in 100 ml THF was irradiated with the 140 watt source at room temperature without bubbling nitrogen gas through the mixture. After 5.5 hours, by which time 100 ml gas had been evolved from the reaction mixture, 75 ml heptane was added to the solution, and the total volume was concentrated on a rotary evaporator to about 60 ml. Cooling to -20° precipitated pale yellow crystals of *cis*-$CpMn(CO)_2(GePh_3)H$ (0.31 g, 17%).

Synthesis of *trans*-$CpRe(CO)_2(SnPh_3)_2$

A solution of $CpRe(CO)_3$ (1.0 g, 3.0 mmol) and Ph_3SnH (2.1 g, 6.0 mmol) in 200 ml petroleum ether was irradiated with the 450 watt source for 23 hours. The solution and solid residues washed out with dichloromethane were combined and the mixture was reduced to dryness on a rotary evaporator. Unreacted $CpRe(CO)_3$ was sublimed off, and the residue in a small amount of 1:1 petroleum ether: dichloromethane was adsorbed onto 100 g silicic acid. Elution by suction filtration with 300 ml petroleum ether and 100 ml of a 1:1 mixture of petroleum ether:dichloromethane removed most of the $CpRe(CO)_3$. Further elution with 200 ml acetone led to a solution containing the product and a small amount of $CpRe(CO)_3$ which was sublimed off after removal of the solvent. Recrystallization of the residue from dichloromethane-heptane gave pale brown crystals of *trans*-$CpRe(CO)_2(SnPh_3)_2$ (50 mg, 1.7%).

Synthesis of *trans*-$CpRe(CO)_2(GePh_3)Me$

A THF solution of Ph_3GeLi was prepared by combining *n*-C_4H_9Li (4 ml, 0.625 M in hexane, 2.5 mmol) and Ph_3GeH (0.762 g, 2.5 mmol) in 150 ml THF, and stirring for two hours. The solution was combined with $CpRe(CO)_3$ (0.84 g, 2.5 mmol) in 50 ml THF, and irradiated with the 450 watt source for 31 hours. The THF solution was placed in a round-bottomed flask, after which excess $\mathrm{CH_3I}$ was added. After stirring for three hours, the solution was evaporated to dryness and the residue recrystallized from dichloromethane-heptane, affording a very small amount of *trans*-$\mathrm{CpRe(CO)_2(GePh_3)Me}$, identified by infrared and mass spectra. The amount of brown crystalline solid was not sufficient for microanalysis.

Synthesis of *trans*-$\mathrm{CpRe(CO)_2(GeCl_3)_2}$

A solution of $\mathrm{CpRe(CO)_3}$ (0.335 g, 1.00 mmol) and $\mathrm{Cl_3GeH}$ (1.84 g, 10.0 mmol) in 10 ml hexane was stirred for one hour. Excess $\mathrm{Cl_3GeH}$ was destroyed by reaction with 20 ml methanol and then solvents were removed *in vacuo*. Extraction of the residue with 100 ml hot heptane and cooling the extract to -20° afforded white crystals of *trans*-$\mathrm{CpRe(CO)_2(GeCl_3)_2}$ (0.2 g, 30%).

Synthesis of *trans*-$\mathrm{CpMn(CO)_2(GeCl_3)_2}$

A solution of $\mathrm{CpMn(CO)_3}$ (1.0 g, 5.0 mmol) and $\mathrm{Cl_3GeH}$ (9.2 g, 50 mmol) in 100 ml heptane was irradiated with the 140 watt source at room temperature for seven hours. After irradiation, 20 ml methanol was added to destroy excess $\mathrm{Cl_3GeH}$, and then solvents were removed *in vacuo*. Extraction of the residue with 100 ml hot heptane and cooling the extract to -20° afforded 0.46 g of crude product (17%). A second recrystallization from hot heptane gave an analytical sample of pale yellow *trans*-$\mathrm{CpMn(CO)_2}$-

$(GeCl_3)_2$.

Synthesis of *trans*-$C_6H_6Cr(CO)_2(GeCl_3)_2$

A solution of $C_6H_6Cr(CO)_3$ (0.21 g, 1.0 mmol) and Cl_3GeH (0.90 g, 5.0 mmol) in 60 ml petroleum ether was irradiated with the 140 watt source at room temperature for 40 hours. The solution was filtered and evaporated to dryness on a rotary evaporator. Crystallization of the oily residue from dichloromethane-heptane at -20° afforded yellow-orange crystals of $C_6H_6Cr(CO)_2(GeCl_3)_2$ (0.11 g, 20%).

Synthesis of *trans*-$CpRe(CO)_2(GeEtCl_2)_2$

A solution of $CpRe(CO)_3$ (0.43 g, 1.3 mmol) and $EtCl_2GeH$ (1.0 g, 5.8 mmol) in 200 ml heptane was irradiated with the 450 watt source for one hour. The reaction mixture was reduced to dryness and the residue was chromatographed on Florisil. Elution with dichloromethane gave a narrow red-brown band. Removal of solvent from the resulting solution gave a small amount of red-brown solid, whose infrared and mass spectra characterized it as *trans*-$CpRe(CO)_2(GeEtCl_2)_2$. The amount obtained was insufficient for microanalysis.

Synthesis of $[Et_4N][CpRe(CO)_2GeCl_3]$

A solution of $CpRe(CO)_3$ (2.45 g, 7.35 mmol) and $[Et_4N][GeCl_3]$ (5.55 g, 18.0 mmol) in 300 ml THF was irradiated at reflux temperature with the 140 watt source for 26 hours. After irradiation, the solution was reduced in volume to about 20 ml on a rotary evaporator and 75 ml methanol was then added. Cooling to -20° afforded 2.04 g of yellow crystals after filtering, washing with cold methanol, and drying *in vacuo*. Reducing the volume of the mother liquor to about 30 ml afforded a second crop of 0.44 g (total yield 55%). Other preparations of $[Et_4N][CpRe(CO)_2GeCl_3]$ gave yields varying from 39-66%.

Synthesis of $[Et_4N][CpRe(CO)_2GeBr_3]$

A solution of $CpRe(CO)_3$ (3.0 g, 9.0 mmol) and $[Et_4N][GeBr_3]$ (7.8 g, 18 mmol) in 250 ml THF was irradiated at reflux temperature with the 140 watt source for 72 hours. After irradiation, the solution was reduced in volume to about 15 ml, and then 10 ml methanol was added. The solution was cooled, and then 100 ml cold diethyl ether was added to precipitate the crude product. Recrystallization was effected by dissolving the product in dichloromethane, filtering off unreacted $[Et_4N][GeBr_3]$, adding a small amount of methanol, and then reducing the volume of solvent to about 40 ml. Cooling to -20° for 48 hours afforded 2.24 g (33%) of yellow $[Et_4N]$-$[CpRe(CO)_2GeBr_3]$.

Synthesis of $[Et_4N][CpRe(CO)_2SnCl_3]$

The same method as for the preparation of $[Et_4N]$-$[CpRe(CO)_2GeCl_3]$ was used. Irradiation of a mixture of $CpRe(CO)_3$ (2.5 g, 7.4 mmol) and $[Et_4N][SnCl_3]$ (6.2 g, 18 mmol) in 200 ml THF for 30 hours produced, after crystallization, 3.6 g (73%) of yellow $[Et_4N][CpRe(CO)_2SnCl_3]$.

Synthesis of $[Et_4N][C_6H_6Cr(CO)_2GeCl_3]$

A mixture of $C_6H_6Cr(CO)_3$ (2.14 g, 10.0 mmol) and $[Et_4N][GeCl_3]$ (6.2 g, 20 mmol) in 200 ml THF was irradiated with the 450 watt source for two hours. After irradiation the solution was filtered and reduced in volume to about 10 ml. Addition of 150 ml methanol produced small red crystals of product.The crystals were filtered off and the mother liquor was concentrated and cooled to -20° to produce a second crop of crystals. The total yield of $[Et_4N][C_6H_6Cr(CO)_2GeCl_3]$ was 3.76 g (76%). A microanalytical sample was prepared by recrystallization from dichloromethane-methanol.

Synthesis of $[Et_4N][C_6H_6Cr(CO)_2SnCl_3]$

The same procedure as for $[Et_4N][C_6H_6Cr(CO)_2GeCl_3]$ was used. Irradiation of $C_6H_6Cr(CO)_3$ (1.3 g, 6.0 mmol) and $[Et_4N][SnCl_3]$ (2.8 g, 8.0 mmol) in 200 ml THF for 45 minutes produced after crystallization, 2.5 g (77%) of red $[Et_4N][C_6H_6Cr(CO)_2SnCl_3]$.

Synthesis of *trans*-$CpRe(CO)_2(GeBr_3)H$

To a rapidly stirred solution of $[Et_4N][CpRe(CO)_2GeBr_3]$ (1.1 g, 1.5 mmol) in 10 ml dichloromethane in a Schlenk tube was added dropwise 3 ml phosphoric acid. Stirring was continued for 2.5 hours, after which the bottom of the tube was cooled to about -78°. As soon as the acid had solidified, and suspended solids had settled to the bottom, the dichloromethane solution was syringed into another Schlenk tube. Cooling of this solution by slow immersion into a dry ice-acetone bath initiated crystallization. Addition of small amounts of heptane to the cold solution completed crystallization and afforded pale brown crystals of *trans*-$CpRe(CO)_2(GeBr_3)H$ (0.49 g, 53%). Further purification for microanalysis or spectra was not necessary.

Synthesis of other hydrides and deuterides

The same method as for *trans*-$CpRe(CO)_2(GeBr_3)H$ was used for the hydrides *trans*-$CpRe(CO)_2(ECl_3)H$ and the deuterides *trans*-$CpRe(CO)_2(GeX_3)D$ (X = Cl, Br). Phosphoric acid-d_3 was used for deuteration. Concentrations of at least 0.1 M $[Et_4N][CpRe(CO)_2(EX_3)]$ in dichloromethane should be used to aid crystallization (see Results and Discussion, Part B, section 2). Yields of the hydrides and deuterides varied from 20-60%.

Synthesis of *trans*-$CpRe(CO)_2(GeCl_3)Cl$

Method A

To a rapidly stirred mixture of $[Et_4N][CpRe(CO)_2GeCl_3]$ (0.42 g, 0.68 mmol) in 10 ml benzene was added *n*-$C_4H_9OSO_2Cl$ (0.52 g, 3.0 mmol). After stirring for 15 minutes, during which solid $[Et_4N][CpRe(CO)_2GeCl_3]$ gradually disappeared, the solvent was removed under vacuum, and the residue recrystallized from dichloromethane-heptane, affording yellow, crystalline *trans*-$CpRe(CO)_2(GeCl_3)Cl$ (0.18 g, 59%).

Method B

A mixture of $[Et_4N][CpRe(CO)_2GeCl_3]$ (0.43 g, 0.70 mmol) and $MeOSO_2Cl$ (0.45 g, 3.4 mmol) was stirred in 10 ml dichloromethane for two hours, after which 5 ml petroleum ether was added and the solution cooled to -20°. The white precipitate which formed was filtered off, and 5 ml petroleum ether was added to the filtrate. Cooling to -20° afforded yellow crystals of *trans*-$CpRe(CO)_2(GeCl_3)Cl$ (0.22 g, 60%).

Method C

Chlorine gas was bubbled rapidly through a solution of $[Et_4N][CpRe(CO)_2GeCl_3]$ (0.20 g, 0.32 mmol) in 20 ml dichloromethane for two minutes. Removal of solvent on a rotary evaporator and sublimation with decomposition at 80° (0.02 mm) yielded 0.035 g (21%) of microcrystalline *trans*-$CpRe(CO)_2(GeCl_3)Cl$.

Synthesis of *trans*-$CpRe(CO)_2(GeCl_3)Br$

A solution of $[Et_4N][CpRe(CO)_2GeCl_3]$ (0.30 g, 0.49 mmol) and bromine (0.030 ml, 0.55 mmol) in 10 ml dichloromethane was stirred for ten minutes. Crystallization was effected by adding cold diethyl ether (10 ml), and then cold petroleum ether. Subsequent cooling to -20° gave 0.21 g (75%) of orange *trans*-$CpRe(CO)_2(GeCl_3)Br$. An analytical sample was prepared by sublimation at 75° (0.02 mm).

Synthesis of *trans*-CpRe(CO)$_2$(GeBr$_3$)Br

A solution of [Et$_4$N][CpRe(CO)$_2$GeBr$_3$] (0.62 g, 1.0 mmol) and bromine (0.32 g, 2.0 mmol) in 20 ml dichloromethane was stirred for five minutes, and then the solvent was removed on a rotary evaporator. Crystallization of the resulting oil from a small amount of methanol at -20° yielded 0.27 g (39%) of yellow *trans*-CpRe(CO)$_2$(GeBr$_3$)Br.

Synthesis of *trans*-CpRe(CO)$_2$(GeCl$_3$)I

A solution of [Et$_4$N][CpRe(CO)$_2$GeCl$_3$] (0.20 g, 0.32 mmol) and iodine (0.089 g, 0.35 mmol) in 10 ml dichloromethane was stirred for 30 minutes. Heptane (20 ml) was then added, and about 10 ml solvent was removed at reduced pressure. Cooling to -20° yielded, in two fractions, 0.196 g (98%) of orange *trans*-CpRe(CO)$_2$(GeCl$_3$)I.

Synthesis of *trans*-CpMn(CO)$_2$(SnCl$_3$)$_2$

A solution of [Et$_4$N][CpMn(CO)$_2$SnCl$_3$] (0.60 g, 1.1 mmol) and SnCl$_4$ (1.3 g, 5.0 mmol) in 10 ml dichloromethane was stirred for one hour. The white precipitate was filtered off, and the filtrate cooled to -20°, affording brown crystals of crude product. Recrystallization from methanol at -20° yielded 30 mg (4%) of orange *trans*-CpMn(CO)$_2$(SnCl$_3$)$_2$.

Synthesis of *trans*-CpRe(CO)$_2$(SnCl$_3$)Cl

Method A

To a solution of [Et$_4$N][CpRe(CO)$_2$SnCl$_3$] (1.0 g, 1.5 mmol) in 15 ml dichloromethane was added MeOSO$_2$Cl (2.0 g, 15 mmol). The solution was stirred for two minutes and then about 8 ml solvent was removed at reduced pressure. Addition of 8 ml methanol and cooling to -78° precipitated a white powder, which was filtered off. Addition of 10 ml diethyl ether to the filtrate and cooling to -78° afforded 0.012 g (1.4%) of analytically pure, yellow *trans*-$CpRe(CO)_2(SnCl_3)Cl$.

Method B

Chlorine gas was bubbled slowly through a solution of $[Et_4N][CpRe(CO)_2SnCl_3]$ (1.0 g, 1.5 mmol) in 40 ml dichloromethane for 15 minutes. Stirring was continued for 30 minutes, after which the solution was filtered. Addition of 20 ml petroleum ether to the filtrate, and the removal of about 20 ml solvent by bubbling nitrogen gas through the mixture afforded, on cooling to -20°, 0.40 g (50%) of crude product, identified by infrared and mass spectra.

Synthesis of *trans*-$CpRe(CO)_2I_2$

A solution of $[Et_4N][CpRe(CO)_2SnCl_3]$ (0.66 g, 1.0 mmol) and iodine (0.25 g, 1.0 mmol) in 15 ml dichloromethane was stirred for one hour. Addition of 10 ml petroleum ether, removal of a small amount of solvent at reduced pressure, and cooling to -20° yielded red-brown crystals of *trans*-$CpRe(CO)_2I_2$ (0.17 g, 30%). An analytical sample was prepared by sublimation at 80° (0.02 mm).

Synthesis of *cis*-$CpRe(CO)_2Cl_2$

A solution of *trans*-$CpRe(CO)_2(SnCl_3)Cl$ (0.40 g, 0.70 mmol) in 20 ml methanol was heated in a sealed Carius tube at 80° for 16 hours. After opening the tube, the solution was removed and cooled to -78°. Orange-brown microcrystals of product precipitated. The solid was recrystallized from dichloromethane-heptane, affording 0.020 g (8%) of orange *cis*-$CpRe(CO)_2Cl_2$.

Synthesis of *trans*-$CpRe(CO)_2[Ge(OMe)Cl_2]Cl$

A crude sample of *trans*-$CpRe(CO)_2(GeCl_3)Cl$, prepared by evaporating the solvent from a mixture of $[Et_4N]$-$[CpRe(CO)_2GeCl_3]$ (0.35 g, 0.56 mmol) and $MeOSO_2Cl$ (0.59 g, 4.6 mmol) in acetone, was refluxed in excess methanol for one hour. Concentrating the solution and then cooling to -78° afforded 0.14 g (54%) of yellow *trans*-$CpRe(CO)_2[Ge(OMe)Cl_2]Cl$.

Synthesis of *trans*-$CpRe(CO)_2[Ge(OEt)Cl_2]Cl$

A solution of *trans*-$CpRe(CO)_2(GeCl_3)Cl$ (0.40 g, 0.77 mmol) was refluxed in 25 ml ethanol. After two hours, the solution was cooled to -78°, affording 0.21 g (51%) of yellow *trans*-$CpRe(CO)_2[Ge(OEt)Cl_2]Cl$. An analytical sample was prepared by sublimation at 80° (0.02 mm) for 24 hours.

Synthesis of *trans*-$CpRe(CO)_2(GeCl_3)Me$

A mixture of $[Et_4N][CpRe(CO)_2GeCl_3]$ (0.72 g, 1.2 mmol) and $MeOSO_2F$ (0.30 g, 2.6 mmol) in 10 ml toluene was rapidly stirred for eight hours. The fine white precipitate was filtered off and heptane was added to the filtrate until turbidity occurred. Cooling slowly to -78° afforded pale brown crystals of *trans*-$CpRe(CO)_2(GeCl_3)Me$ (0.41 g, 58%).

Synthesis of $CpRe(CO)_2SO_2$

A solution of $[Et_4N][CpRe(CO)_2GeCl_3]$ (1.2 g, 2.0 mmol) and $MeOSO_2F$ (0.46 g, 4.0 mmol) was stirred in 30 ml acetone for one hour. Solvent was removed and the orange-black residue was dried *in vacuo* for 24 hours. Sublimation at 90° (0.02 mm) for five days afforded a yellow powder on the probe, consisting of 0.44 g (60%) of $CpRe(CO)_2SO_2$. An analytical sample was prepared by recrystallization from dichloromethane-heptane at -20°.

Synthesis of $C_6H_6Mn(CO)_2GeCl_3$

A solution of $[C_6H_6Mn(CO)_3][PF_6]$ (0.36 g, 1.0 mmol) and $[Et_4N][GeCl_3]$ (3.4 g, 1.1 mmol) in 10 ml acetone was stirred at room temperature for three hours, after which gas bubbles no longer formed in the solution. The acetone was removed and the yellow residue recrystallized twice from dichloromethane at -78°, affording 0.36 g (97%) of slightly impure orange crystals. An analytical sample of $C_6H_6Mn(CO)_2GeCl_3$ was prepared by sublimation of a small amount of impure product at 100° (0.02 mm) for seven days.

CHAPTER IV

SYNTHESIS AND PROPERTIES OF SOME RHENIUM AND IRON ALLYL COMPOUNDS

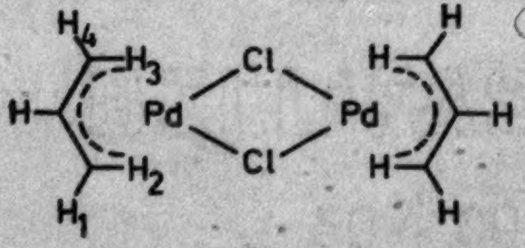
INTRODUCTION

The allyl ligand may form both 1-η- and 1-3-η-bonds (σ and π, respectively, will be used for convenience) with transition metals. The formation of π-allyl complexes is now known for all the transition metal triads from titanium to nickel, and a number of reviews have discussed their synthesis and properties.[228-232]

Up to the present time there have been few π-allyl complexes of the manganese triad, and they are generally of the form (π-allyl)M$(CO)_4$ (M = Mn, Re). A recent paper described the synthesis of a number of these manganese and rhenium complexes, which had previously been prepared in poor yields.[233]

Interest in allyl complexes stems from a number of sources: (i) homogeneous catalytic activity shown by some π-allyl complexes in reactions of unsaturated hydrocarbons,[229] (ii) unusual structural features of the allyl-metal bond, (iii) unusual spectral features of the π-allyl ligand, and (iv) stereochemical non-rigidity in π-allyl complexes.

The structural features of interest lie in the variation of metal-carbon bond distances in the metal-allyl bond,[234,235] and in the variation in the angle between the allyl plane and the plane defined by the two outer carbon atoms and the metal atom.[234] These features have been studied by X-ray crystallography in order to clarify the nature of the bonding between the metal and the allyl ligand.[236] Nmr spectroscopy has also proved to be a powerful tool for the investigation of those points of interest in (iii) and (iv) above. In symmetrically bonded complexes such as $(C_3H_5PdCl)_2$* the *syn* protons (1 and 4 in 31) are equivalent, as are the *anti* protons (2 and 3), in the nmr spectrum.[237] On the other hand, separate signals for each methylene proton in the allyl ligand were exhibited by $(2\text{-}C_4H_7)Pd(PPh_3)Cl$,[238] 32.



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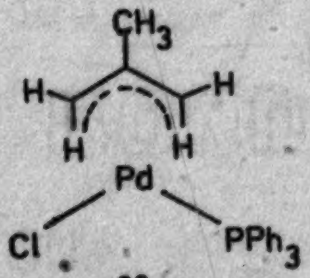

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Other work employing nmr spectroscopy involved the study of conformational rearrangements of the allyl group on coordination of donor ligands to the complex,[239] and the study of orientations of the allyl ligand with respect to other groups on the metal.[240] Finally, stereochemical

*In this chapter, the following abbreviations will be used: $C_3H_5 = \eta\text{-}C_3H_5$, $n\text{-}C_4H_7 = 1\text{-}3\text{-}\eta\text{-}n\text{-}(CH_3)C_3H_4$, n = 1,2 (position of methyl substitution).

non-rigidity of π-allyl complexes has recently received much attention.[89,90,232] Variable temperature proton nmr spectroscopy has provided evidence for σ-π processes,[89] rotation about the allyl-metal axis,[241] left-to-right exchange,[242] and *syn-anti* exchange.[242]

The present study was undertaken to determine whether allyl derivatives of $CpM(CO)_3$ could be prepared, and if so, what physical and chemical properties they would have.

In the Results and Discussion, the synthesis and chemical properties of the new compounds derived from $CpRe(CO)_3$ will be discussed in Part A. The nmr spectra of these derivatives will be interpreted in Part B. Part C will deal with the preparation and properties of the iron complex, $(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$. Finally, Part D will present an outline for further research into π-allyl derivatives of $CpRe(CO)_3$.

RESULTS AND DISCUSSION

A. Synthesis of the π-Allyl Rhenium Complexes

1. Chloride and Bromide Derivatives

The photochemical reactions between $CpRe(CO)_3$ and C_3H_5Cl, C_3H_5Br, and 2-MeC_3H_4Cl proceed by the elimination of two molecules of carbon monoxide to produce the corresponding rhenium allyl derivatives:

$$CpRe(CO)_3 + (allyl)X \xrightarrow{h\nu} Cp(\pi\text{-allyl})Re(CO)X + 2CO \quad (IV\text{-}1)$$

The oxidative eliminations occurred over periods of one to eight hours in hydrocarbon solvents, affording yields varying from 10 to 40 percent. The first step in the reactions is probably photochemically-induced loss of carbon monoxide from $CpRe(CO)_3$, analogous to reaction III-3. Addition of an allyl halide molecule to the unsaturated species would lead to the formation of a σ-allyl complex:

$$[CpRe(CO)_2]^* + (allyl)X \rightarrow Cp(\sigma\text{-allyl})Re(CO)_2X \quad (IV\text{-}2)$$

Since infrared spectra of reaction mixtures of the two starting materials showed no bands which could be assigned to such a σ-allyl complex, loss of another carbonyl ligand from the rhenium species must be concurrent with or follow immediately after addition of allyl halide:

$$Cp(\sigma\text{-allyl})Re(CO)_2X \rightarrow Cp(\pi\text{-allyl})Re(CO)X + CO \quad (IV\text{-}3)$$

This facile formation of a rhenium π-allyl complex should be contrasted with the reaction between allyl halide and the rhenium pentacarbonyl anion:

$$Na[Re(CO)_5] + C_3H_5Cl \rightarrow (\sigma\text{-}C_3H_5)Re(CO)_5 \qquad \text{(IV-4)}$$

The product is reported not to undergo conversion to $(\pi\text{-}C_3H_5)Re(CO)_4$, either by heat or irradiation.[243] The manganese analogue, $(\sigma\text{-}C_3H_5)Mn(CO)_5$, undergoes decarbonylation with ultraviolet light to give $(\pi\text{-}C_3H_5)Mn(CO)_4$.[244]

Irradiation of a hydrocarbon solution of $CpMn(CO)_3$ and $2\text{-}MeC_3H_4Cl$ or C_3H_5Br led only to a black decomposition product, insoluble in hydrocarbons and dichloromethane. The fact that little or no $CpMn(CO)_3$ remained after the short irradiation times (30 minutes for C_3H_5Br) suggests that interaction of the allyl halides with the unsaturated manganese complex $[CpMn(CO)_2]^*$ (see reaction III-3) produces a species unstable under the reaction conditions employed. In contrast, other photochemical reactions involving $CpMn(CO)_3$ (e.g. those in Chapter III), when little or no product is obtained, leave significant amounts of unreacted $CpMn(CO)_3$.

The rhenium derivatives produced in reaction IV-1 are reasonably soluble in hydrocarbon solvents, and very soluble in solvents such as diethyl ether, dichloromethane, and acetone. They are stable to air oxidation indefinitely in the solid state, and show no trace of decomposition in solution on exposure to air for a few hours.

The infrared spectra of the allyl halide derivatives exhibit a single band in the carbonyl region. The mass spectra exhibit a molecular ion with the expected isotope combination pattern. The base peak in each spectrum is the peak for the parent ion minus CO. The molecular ion has an intensity about 40 percent of the base peak in each case. Other major peaks in the spectra can be assigned to the ions $CpReX^+$, $CpReC_3H_2^+$ (for C_3H_5 derivatives), and $C_4H_6ReCOCl^+$ (for the C_4H_7 derivative).

2. Reaction with Allyl Iodide

Under the same conditions as for the syntheses of $Cp(C_3H_5)Re(CO)X$ ($X = Cl, Br$) the reaction involving C_3H_5I produced as the major product the diiodide, *trans*-$CpRe(CO)_2I_2$ (see Chapter III, Part D), with the desired allyl derivative as a minor product:

$$CpRe(CO)_3 + C_3H_5I \xrightarrow[\text{methanol or cyclohexane}]{h\nu} \textit{trans}\text{-}CpRe(CO)_2I_2 + Cp(C_3H_5)Re(CO)I \qquad \text{(IV-5)}$$

In a similar reaction carried out in refluxing methanol rather than in cyclohexane at room temperature, a similar ratio of products was obtained, but in lower overall yield.

In the allyl chloride and bromide reactions the dihalide derivatives $CpRe(CO)_2X_2$ were detected in very small amounts, but gave no problems in purification procedures. On the other hand, with allyl iodide, the diiodide complex was obtained in over 50 percent yield, and the ratio of diiodide to allyl complex in the reaction mixtures was estimated to about 3:1 by infrared spectroscopy. Since the allyl derivative could not be isolated free of the diiodide complex by crystallization, sublimation, or chromatography, no analytical data were obtained for this compound. The carbonyl stretching frequency of 1975 cm^{-1} in heptane is close to those of the chloride and bromide analogues, and mass spectra of mixtures of the two products show, besides the spectrum for *trans*-$CpRe(CO)_2I_2$, the molecular ion and fragmentation pattern expected for $Cp(C_3H_5)Re(CO)I$.

In two attempts to prepare $Cp(C_3H_5)Re(CO)I$ free of the diiodide, $Cp(C_3H_5)Re(CO)Cl$ was refluxed for two days with a large excess of sodium iodide in both methanol and acetone. In both cases infrared and mass spectra of reaction residues after removal of solvent showed predominantly starting material, and only a small amount of the desired product.

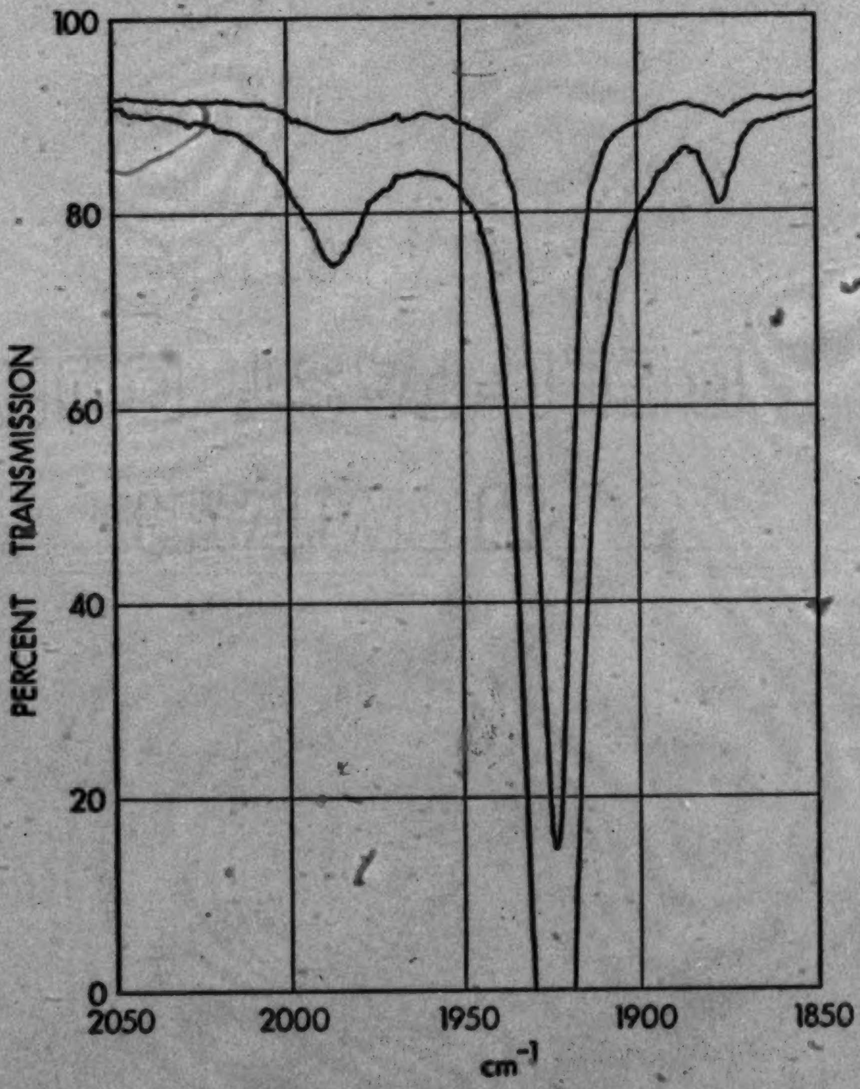
3. The Formation of $Cp(2\text{-}C_4H_7)Re(CO)H$

An attempt to obtain the hydride analogue, $Cp(C_3H_5)Re(CO)H$, by refluxing $Cp(C_3H_5)Re(CO)Cl$ with sodium borohydride in benzene led only to unreacted starting materials. With the more powerful reagent, lithium aluminum hydride, and under conditions favourable for the formation of hydride complexes by this route,[190,245] the derivative Cp$(2\text{-}C_4H_7)$Re(CO)H was obtained from Cp$(2\text{-}C_4H_7)$Re(CO)Cl in moderate yield.

The low-melting crystalline solid, soluble in hydrocarbons as well as in more polar organic solvents, could not be crystallized from cold heptane solutions. Isolation was best carried out by sublimation of the crude oily reaction product onto a water-cooled cold finger *in vacuo*. The pure solid may be recovered from dichloromethane solutions by complete removal of the solvent *in vacuo*.

An infrared spectrum of Cp$(2\text{-}C_4H_7)$Re(CO)H in heptane in the region between 1700 and 2200 cm^{-1} exhibits three bands, $\nu(^{12}C{\equiv}O)$, $\nu(^{13}C{\equiv}O)$, and ν(Re-H) (Fig. 21). The two bands at 1984 and 1924 cm^{-1}, with roughly the same relative intensity, are apparent in a Raman spectrum of the hydride, also recorded in heptane. The strong band at 1924 cm^{-1} is probably the carbonyl stretching band, since the ^{13}C carbonyl stretching frequency, expected to be c. 45 cm^{-1} below this band,[84] appears as a very weak peak at 1877 cm^{-1}. The very weak band at 1984 cm^{-1}, easily visible in more concentrated solutions, is more likely the rhenium-hydrogen stretching band. Formal verification of this assignment, of course, should be made by recording the spectrum of the deuteride, Cp$(2\text{-}C_4H_7)$Re(CO)D, as yet unsynthesized. The shift in the CO stretching frequency on substitution of a hydrogen atom for a halogen atom (Table XVI) clearly demonstrates the ability of the halogens to withdraw electron density from the metal.

The mass spectrum of $Cp(2\text{-}C_4H_7)Re(CO)H$ exhibits a



$Cp(2\text{-}C_4H_7)Re(CO)H$

Figure 21

molecular ion at m/e 336, a peak for parent ion minus carbonyl, and a base peak of nominal mass 304, corresponding to $ReC_9H_9^+$. Other strong peaks can be assigned to $ReC_8H_7^+$ (m/e 290) and $ReC_7H_7^+$ (m/e 278). There was no peak at m/e 280, corresponding to loss of 2-methylpropene from the molecular ion.

As is common for transition metal hydrides,[190] reaction with an organic halide results in cleavage of the metal-hydrogen bond and formation of a metal halide:

$$Cp(2\text{-}C_4H_7)Re(CO)H + CHCl_3 \rightarrow Cp(2\text{-}C_4H_7)Re(CO)Cl + CH_2Cl_2 \qquad \text{(IV-6)}$$

Reaction IV-6 occurred slowly at room temperature, and only a small amount of the rhenium halide product, identified by infrared and nmr spectroscopy, was detected after four hours.

The hydrogen atom bonded to rhenium was not expected to be very acidic, since the rather low carbonyl stretching frequency (1924 cm^{-1}) indicates a large amount of negative charge built up on the rhenium atom via π-donation from the hydrocarbon ligands. Indeed, there was no reaction between $Cp(2\text{-}C_4H_7)Re(CO)H$ and an excess of triethylamine in dichloromethane. Both the $C\equiv O$ and Re-H stretching bands were unaffected by the addition of the base.

4. Attempts to Prepare Other Allyl Derivatives

Phosphine substitution reactions of the carbonyl ligand in $Cp(C_3H_5)Re(CO)Br$ (by triphenylphosphine) and in $Cp(2\text{-}C_4H_7)Re(CO)Cl$ (by trimethylphosphite) under photochemical conditions were unsuccessful. The carbonyl derivatives were irradiated with excess phosphine or phosphite until the carbonyl band was no longer visible in infrared spectra of reaction mixtures. After partial removal of solvent, chromatography, and crystallization, only traces of the rhenium starting material and unreacted phosphine or phosphite were detected.

The photolysis of $CpRe(CO)_3$ in the presence of excess allyl cyanide both at room temperature in heptane and at reflux temperature in THF did not lead to any isolable product. The only compound recovered from these reactions was unreacted $CpRe(CO)_3$.

An attempt to obtain a fluoride analogue, $Cp(2\text{-}C_4H_7)$-$Re(CO)F$, was made by reacting $Cp(2\text{-}C_4H_7)Re(CO)Cl$ with $AgPF_6$. Stirring the reactants together in benzene for 20 hours at room temperature afforded no product which could be identified as the desired fluoride. A proton nmr spectrum of an orange material isolated from the reaction exhibited no resonances, and a mass spectrum of the material contained no fragments expected for a fluoride derivative.

The reaction between $Cp(2\text{-}C_4H_7)Re(CO)Cl$ and $HGeCl_3$ could possibly have led to rhenium-germanium bond formation either by initial protonation at the allyl ligand to afford an ethylene derivative, or by insertion of $GeCl_2$ between the rhenium-chlorine bond to form $Cp(2\text{-}C_4H_7)Re(CO)\text{-}GeCl_3$. In fact, a reaction did take place in dichloromethane, as evidenced by the slow evolution of a gas, but no identifiable product was obtained. Infrared spectra and mass spectra of residues isolated from reaction mixtures did not aid in identifying any products, and no crystalline substance was obtained.

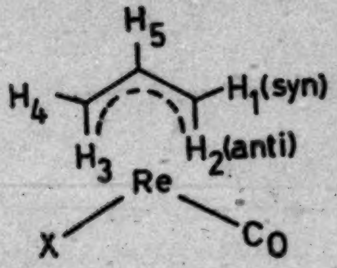
Finally, another attempt to produce an allylrhenium-group IV metal complex, $Cp(C_3H_5)Re(CO)SnMe_3$, was made by photolyzing a mixture of $CpRe(CO)_3$ and allyltrimethyltin, $Me_3SnC_3H_5$, in cyclohexane. In this case the only substance isolated from the reaction mixture was $CpRe(CO)_3$.

B. The Proton NMR Spectra of the Allylrhenium Complexes

1. Halide Derivatives

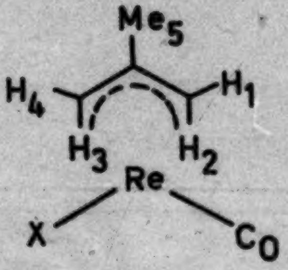
As mentioned in the Introduction, proton nmr spectroscopy has been used to study steric effects on the orientations of the allyl ligand in metal complexes. For example, the two stable conformations of Cp(C_3H_5)Mo$(CO)_2$ were those in which the allyl group was oriented with the central proton towards or away from the cyclopentadienyl ring.[240] The nmr spectrum exhibited one set of resonances for each type of allyl ligand. The infrared spectra of these compounds showed a doubling of the expected number of carbonyl stretching bands due to the two conformations.[246,247] Since only one carbonyl band is exhibited by the infrared spectra of the complexes, Cp(allyl)Re(CO)X, it is likely that only one orientation of the allyl ligand with respect to the cyclopentadienyl group occurs in solution. In confirmation of this, a proton nmr spectrum of Cp(C_3H_5)Re(CO)Br recorded at -75° in CD_2Cl_2 exhibited only one set of peaks for the cyclopentadienyl and allyl groups, and was virtually unchanged from that recorded at ambient temperature.

Since the nmr spectrum of Cp(C_3H_5)Re(CO)Br, 33b, exhibited particularly well-separated resonances and reasonably well-resolved coupling constants, it will be discussed first, and other spectra will be discussed in



33a X = Cl

33b X = Br



34a X = Cl

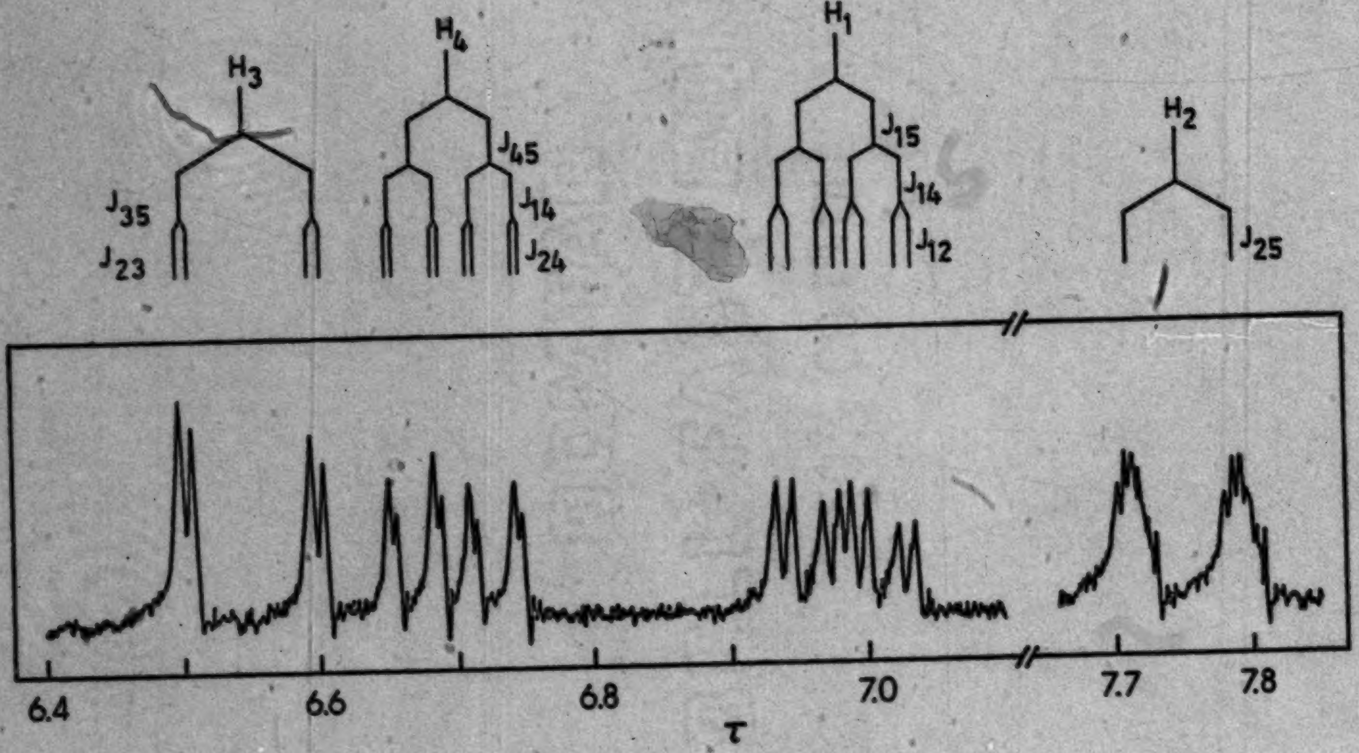
34b X = H_6

Cp rings omitted for clarity

relation to it. The resonances for the allyl protons of 33b are shown in Figures 22 and 23. Coupling constants are shown schematically above the spectrum (in Fig. 22) together with the assignments of the resonances. Chemical shifts and coupling constants are listed in Table XV. The cyclopentadienyl protons for all complexes absorbed at about 4.6 τ.

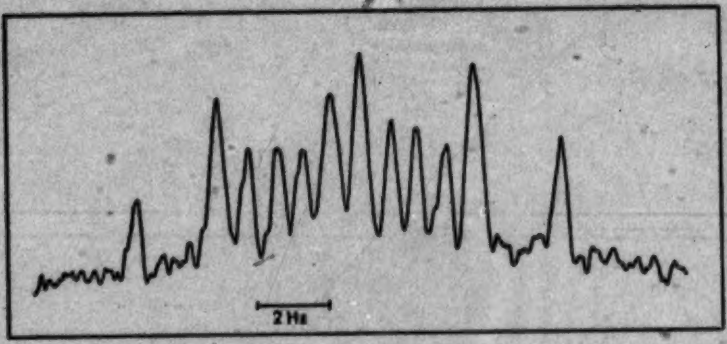
The central proton, H_5, in an unsubstituted allyl group is usually the easiest to assign, since it is split by all *syn* and *anti* protons. Besides having a complex splitting pattern, it usually occurs at lowest magnetic field strength.[232] For 33b, the splitting pattern of twelve lines for H_5 (Fig. 23), centred at 5.63 τ, could be accounted for in a straightforward manner by using the coupling constants (i.e. J_{15}, J_{25}, J_{35}, J_{45}) obtained from the other four resonances.

This spin system can be described as an AA'MM'X system, as opposed to an A_2M_2X pattern seen for other



Methylene Proton Resonances in Cp(C_3H_5)Re(CO)Br

Figure 22 A



Central Proton Resonance (H_5), Centred at 5.63 τ, for $Cp(C_3H_5)Re(CO)Br$

Figure 23

more symmetrical transition metal π-allyl complexes. Central proton resonances have been reported with more than the nine lines predicted by an A_2M_2X treatment in $(C_3H_5)Co(CO)_3$ (11 lines),[248] $[(C_3H_5)PdCl]_2$ (11 lines),[249] and $[(C_3H_5)PdI]_2$ (15 lines).[249] In these cases, second order effects were invoked to explain the extra lines.

In most π-allyl compounds known to date, both *syn* resonances occur at lower field than the *anti* resonances. However, in the present case, it will be seen that the order of one pair of *syn-anti* resonances is reversed. The differentiation between the *syn* and *anti* proton resonances was made almost solely on the basis of coupling constants to the central proton, H_5. In all π-allyl complexes known to date the order of values remains the same as that found for olefins:

$^3J_{HH}(trans) > {}^3J_{HH}(cis) > {}^2J_{HH}(gem)$.[232,249,250]

Therefore the absorptions centred at 6.54 and 7.75 τ (see

Fig. 22) (coupling constants 9.6 and 8.0 Hz) must be due to the *anti* (*trans*) protons, H_2 and H_3, and those at 6.70 and 6.99 τ (coupling constants 6.0 and 5.5 Hz) must be due to the *syn* (*cis*) protons, H_1 and H_4. The *syn* proton at 6.99 τ is clearly coupled to three other protons: the central proton, the geminal proton, and probably the other *syn* proton. The three coupling constants have the values 5.5, 3.4, and 1.2 Hz. From decoupling experiments, the proton at 6.99 τ was found to be split by the *anti* proton at 7.75 τ, but not by that at 6.54 τ. Therefore these two protons (at 6.99 and 7.75 τ) were tentatively assigned as one *syn-anti* pair. Geminal proton coupling, although often zero,[251] has been observed as large as 3.1 Hz (for $Cp(\pi\text{-}1,1\text{-}Me_2C_3H_3)Mo(CO)_2$[241]) and is quite often in the range 1.0-1.5 Hz.[232] Therefore the 1.2 Hz coupling for the *syn* proton at 6.99 τ has been assigned to the geminal proton coupling. The *anti* proton at 7.75 τ is also coupled to the *syn* resonance at 6.70 τ with a coupling constant of only 0.6 Hz; it would be expected that H_2-H_4 (or H_1-H_3) coupling would be of this magnitude[249] (*vide infra*).

The high field *syn-anti* pair of protons has been assigned to H_2 and H_1, respectively, i.e. *cis* to the carbonyl in 33b, since they lie in the normal order (*anti* proton at higher field) and usual positions for π-allyl transition metal carbonyl compounds. For example, the *syn* and *anti* resonances in $Cp(C_3H_5)Mo(CO)_2$[241,247] (high and low temperature spectra) occur at 7.0-7.6 τ, and 8.3-9.1 τ, respectively, and those in $C_3H_5Mn(CO)_4$[248] and $C_3H_5V(CO)_5$[252] occur in the regions 7.3-7.5 τ and 8.2-8.3 τ, respectively. These values should be contrasted with those of the two rotational isomers of $C_3H_5Fe(CO)_3Br$[253] (in CS_2), the *syn* protons at 5.78 and 6.12 τ, the *anti* protons at 6.65 and 7.48 τ; and $C_3H_5W(CO)_4Br$, the *syn* protons at 6.16 -6.89 τ, and the *anti* protons at 6.87-7.83 τ.[254] The presence of halogen ligands in many other complexes similarly causes a deshielding of the allyl resonances.[232]

One might also consider systems where a π-allyl ligand is bonded to an asymmetric transition metal moiety. In π-RC_3H_4PdClL complexes (R = H, Me, L = tertiary phosphine), the *syn-anti* proton pair absorbing at weaker magnetic fields was assigned to a position *trans* to the phosphine ligand, because of the existence of phosphorus-proton coupling,[255,256] and also because of the longer palladium-carbon bond distance *trans* to phosphorus[257] (cf. the crystal structure of $(2\text{-}C_4H_7)Pd(PPh_3)Cl$[258]). If one assumes that changing a phosphine to a carbonyl ligand, and changing from a square planar to a pseudo square pyramidal structure does not reverse deshielding effects on the allyl ligand, then the assignments in Table XV follow from the above arguments.

The *syn-syn* proton coupling constants, J_{14}, of 3.9

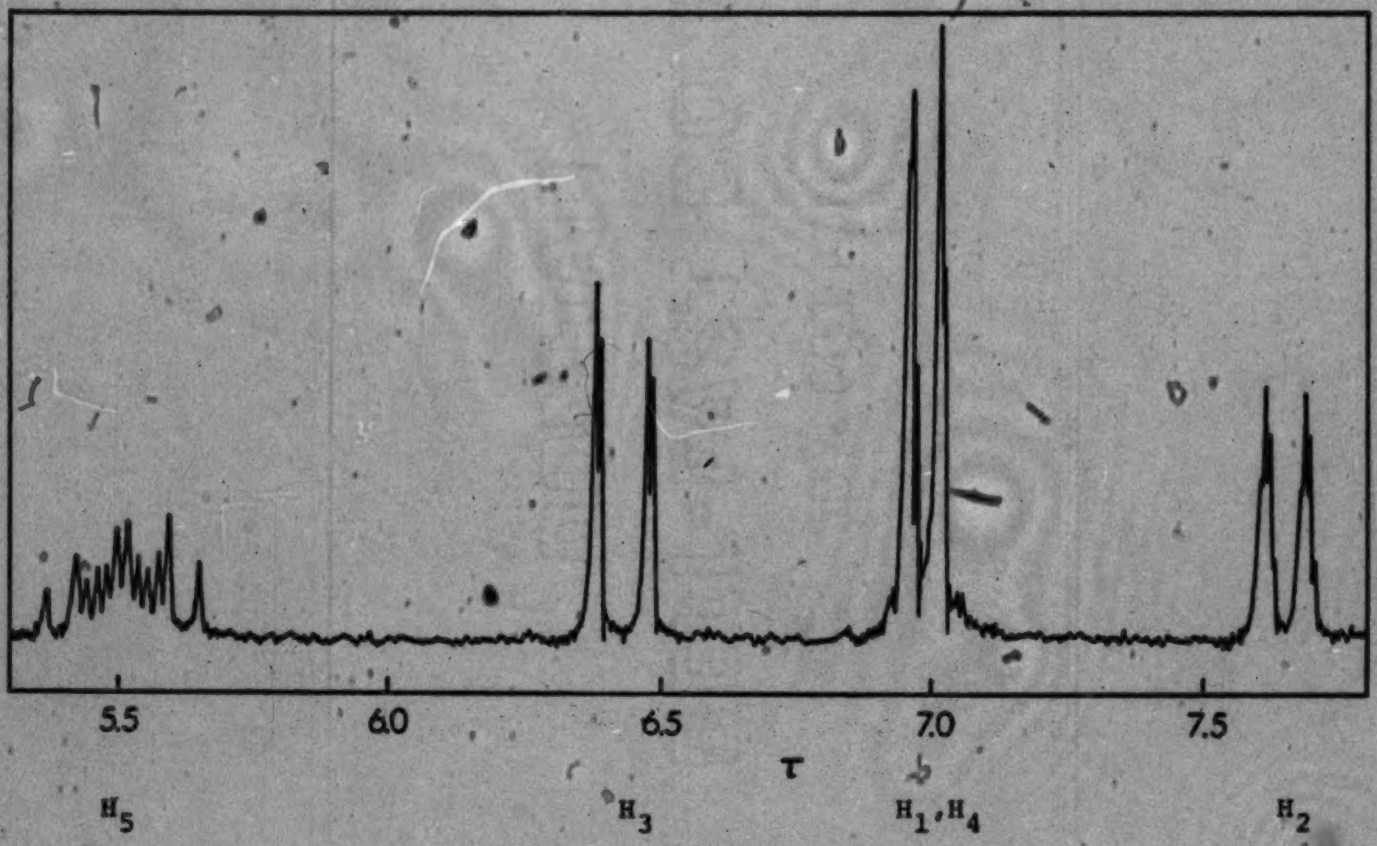
and 3.4 Hz for Cp(2-C_4H_7)Re(CO)Cl, 34a, and Cp(C_3H_5)Re(CO)Br, 33b, respectively, are probably the largest such constants known for a transition metal π-allyl complex. The palladium complexes, (2-ClC_3H_4)Pd-[MeC(O)CHC(O)Me] and Cp(2-C_4H_7)Pd exhibited *syn-syn* proton coupling constants of 2.7 and 2.8 Hz, respectively;[249] a value of 2.9 Hz was found for (2-C_4H_7)Pd(PPh_3)Cl.[257] A large number of other constants between these protons have values typically between 1.0 and 2.0 Hz.[242]

Further decoupling experiments showed that the proton at 7.75 τ, H_2, was coupled to H_3 at 6.54 τ, and possibly to H_4 at 6.70 τ. Since the two larger couplings at H_4 are due to J_{45} and J_{14}, and H_4 was not coupled to H_3, the coupling of 0.6 Hz must indeed be between H_2 and H_4. The three small couplings to H_2 by the other methylene protons account for the broad, unresolved appearance for the doublet at 7.75 τ (Fig. 22). The long range couplings, J_{23} and J_{24}, are not usually observed in allyl metal complexes. The coupling constants corresponding to J_{23} and J_{24} in (π-2-ClC_3H_4)Pd-[MeC(O)CHC(O)Me] were 0.5 and 0.2 Hz, respectively, and in (π-1-PhC_3H_4)Pd[MeC(O)CHC(O)Me] (Ph in H_4 position) the constants were 1.0 and 0.4 Hz, respectively.[249] The coupling constants found in this work for the unsymmetrical allylrhenium halides are of similar size, within experimental error.

In the nmr spectrum of $Cp(C_3H_5)Re(CO)Cl$ it should first be noted that the chemical shifts of the two *syn* protons, H_1 and H_4, are almost degenerate (Fig. 24). Only one doublet (of intensity two, and with each half unsymmetrically split) is exhibited for these protons, centred at 7.00 τ. The *anti* protons again have the large coupling constants to H_5 (7.3 and 10.1 Hz).

The *syn* proton coupling constants to the central proton, J_{15} and J_{45}, are about 5.0 Hz, and their mutual coupling constant, J_{14}, was not measurable. The *anti* proton *cis* to the halogen, H_3 in 33a, was assigned to the low-field resonance, at 6.43 τ, as before; the central proton, H_5, is split into twelve lines as for the bromide analogue.

For $Cp(2\text{-}C_4H_7)Re(CO)Cl$, the four methylene protons were assigned in the same order of chemical shift as for $Cp(C_3H_5)Re(CO)Br$. The methyl group appeared as a singlet at 7.32 τ. Only two coupling constants were measurable, the *syn-syn* constant, J_{14} (3.9 Hz), and the geminal constant, J_{12} (1.2 Hz).

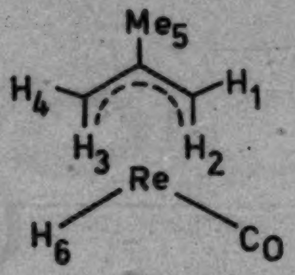


Allyl Proton Resonances in $Cp(C_3H_5)Re(CO)Cl$

Figure 24

2. The Proton NMR Spectrum of $Cp(2\text{-}C_4H_7)Re(CO)H$

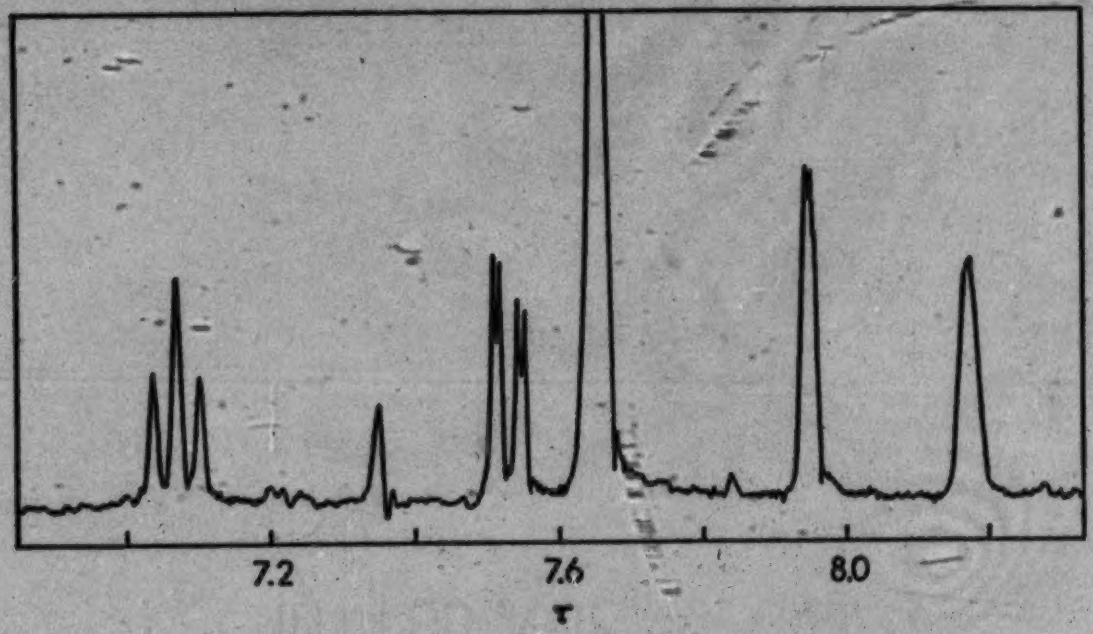
The spectrum of the allylrhenium hydride, 34b,

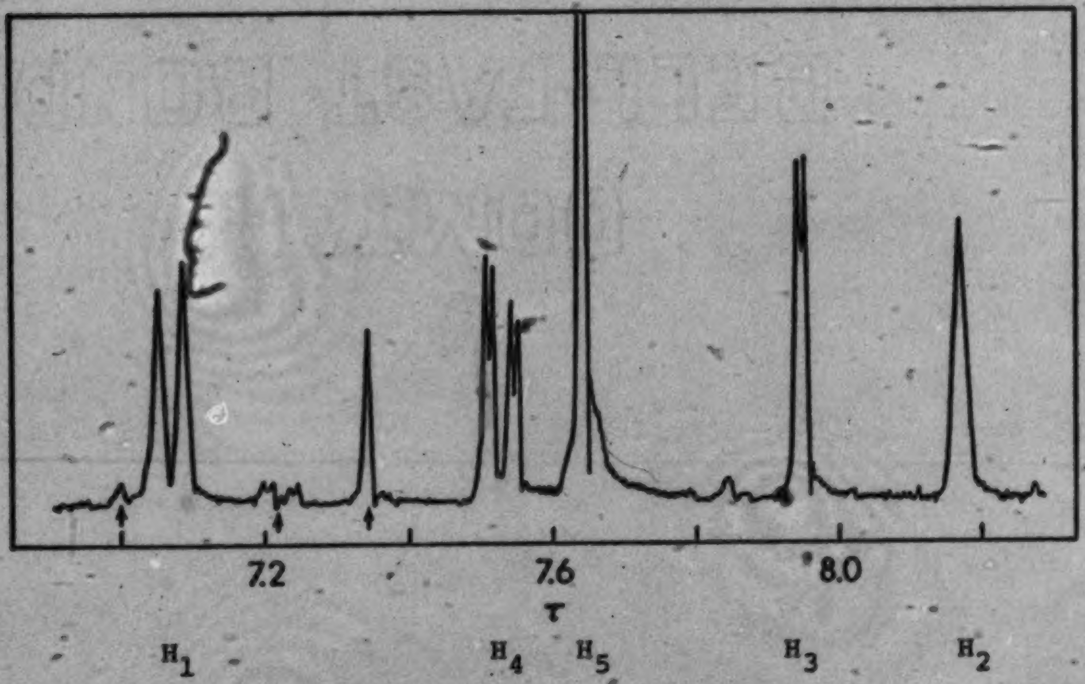


34b

exhibited individual resonances for each *syn* and *anti* proton on the allyl ligand (Fig. 25) as well as singlets for the cyclopentadienyl and methyl protons. The hydrogen atom bonded to rhenium absorbed at 21.94 τ, (Fig. 27), and occurred as a doublet due to coupling to one of the *syn* protons (*vide infra*). The chemical shifts and coupling constants are given in Table XV. It should be noted that peaks due to the formation of $Cp(2\text{-}C_4H_7)Re(CO)Cl$ from $CHCl_3$ and $Cp(2\text{-}C_4H_7)Re(CO)H$ as in reaction IV-6 are visible in Figures 25 and 26.

The two allyl resonances occurring at lowest field were assigned to the *syn* protons, in keeping with the usual order of resonances for allyl complexes without "unusual" perturbing groups (e.g. halogen atoms sometimes reverse the order, *vide supra*). The typical *syn*-*syn* proton coupling constant in 34b supports this assignment of the two lowest field allyl resonances (J_{14} = 3.4 Hz). By decoupling the rhenium-bonded proton it was seen that



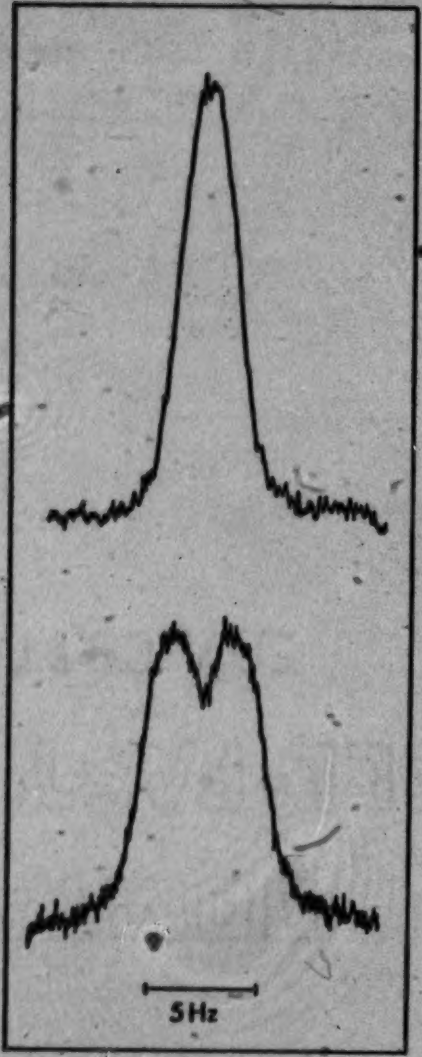


Cp(2-C_4H_7)Re(CO)H, in CD_2Cl_2 with $CHCl_3$ lock.

Peaks marked with arrows are due to Cp(2-C_4H_7)Re(CO)Cl.

Figure 25, above, coupled spectrum.

Figure 26, below, Re-H resonance decoupled.



Re-H Resonance of Cp(2-C_4H_7)Re(CO)H.

Above, peak at 7.07 τ decoupled.

Below, peak at 7.07 τ coupled.

Figure 27

this high-field proton was coupled rather strongly to the lower field *syn* proton (7.07 τ), as well as weakly to the high field *anti* protons (7.95 and 8.17 τ) (cf. Fig. 25 and 26). Conversely, irradiation at a frequency corresponding to 7.07 τ collapsed the rhenium-bonded proton resonance to a singlet (Fig. 27) and similar irradiation at 8.17 τ significantly decreased the linewidth of the high-field doublet; irradiation at 7.54 and 7.95 τ produced no visible change in this doublet. Therefore it is proposed that the allyl protons producing the lowest and highest field resonances (7.07 and 8.17 τ) are bonded to the same carbon atom.

For convenience these protons are labeled H_1 and H_2, *trans* to H_6 in 34b. Whether H_1 and H_2 are, indeed, *trans* (or *cis*) to H_6 cannot be ascertained with present knowledge. Perhaps an X-ray crystallographic and nmr study of a compound such as $Cp(\pi\text{-}1,2\text{-}Me_2C_3H_3)Re(CO)H$, currently unsynthesized, would shed light on the situation.

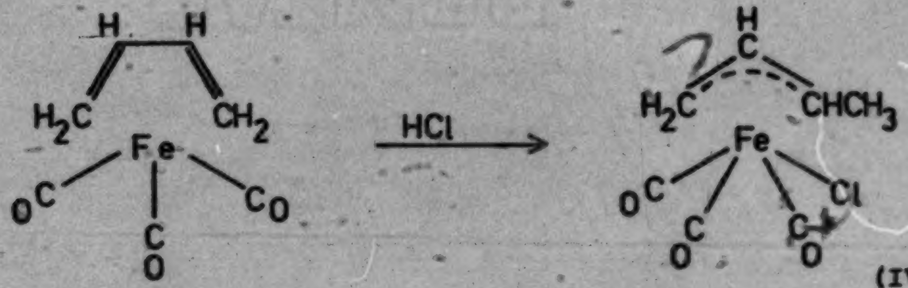
The observed coupling constant through the rhenium atom, J_{16}, was found to be 2.8 Hz. It seems that the only other reported H-H couplings between transition metal hydrides and protons in hydrocarbon ligands occur in η-cyclopentadienyl hydride complexes (1-3 Hz between the hydride and ring protons)[259] and also in $NiH(Me)[P(C_6H_{11})_3]$ (1.6 Hz between the hydride and methyl protons)[260].

The slightly-broadened triplet for H_1, centred at 7.07 τ, is produced by two nearly equal coupling constants to H_4 (J_{14} = 3.4 Hz) and H_6 (J_{16} = 2.8 Hz). Further decoupling experiments indicated significant coupling between H_2 and H_4, and H_3 and H_4. However, because other small couplings among the protons broaden the resonances (especially H_3 and H_2), no accurate coupling constant values could be obtained.

A spectrum of a sample in CD_2Cl_2 recorded at -70° was unchanged from that recorded at ambient temperature. Again, it is likely that only one orientation of the allyl ligand occurs in solution.

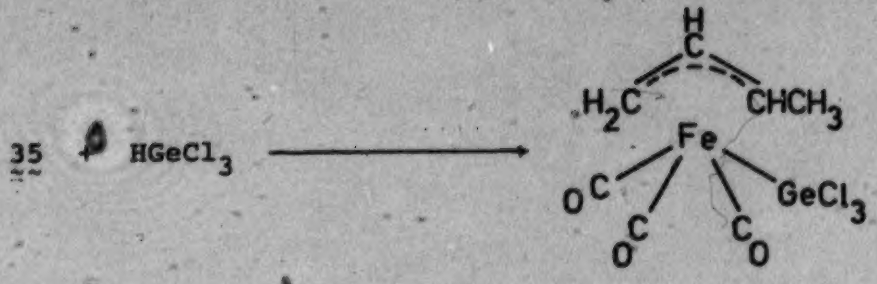
C. Synthesis and Properties of $(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$

In previous work, most other allyliron-group IV metal complexes of the form $(C_3H_5)Fe(CO)_3ER_3$ (E = Si, Ge, Sn, Pb; R = Cl, Br, Me, Ph) were obtained by halide displacement from a group IV halide in reaction with $[(C_3H_5)Fe(CO)_3]^-$.[105] Also, it has long been known that protonation of diene-metal complexes can sometimes lead to π-allyl compounds, e.g.:[261]



35 36 (IV-5)

In the present work, the corresponding reaction between butadiene iron tricarbonyl and trichlorogermane in petroleum ether also led to an allyl complex:



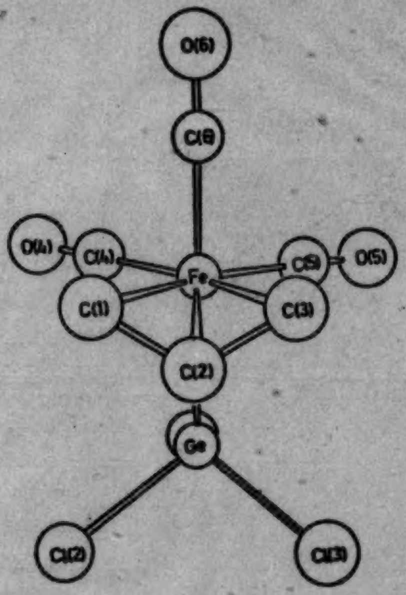
(IV-6)

37

The infrared spectrum of 37 in the carbonyl region exhibits three bands similar to those for $(C_3H_5)Fe(CO)_3$-$GeCl_3$.[105] A recent X-ray crystal study on $(C_3H_5)Fe(CO)_3$-$GeCl_3$[18] has shown that the allyl ligand occupies two coordination sites of an approximately octahedrally-coordinated iron atom (see Fig. 28). The structures for complexes 36 to 40 are not drawn to indicate the actual stereochemistries but only to show the changes in stoichiometry clearly and to facilitate in assigning the proton nmr spectra.

The mass spectrum of $(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$ exhibits a weak molecular ion at a source temperature of 50°. Initial fragmentation consisted of loss of CO or Cl from the molecular ion with about equal frequency. The major peaks in the spectrum, in decreasing intensity, were those due to the ions $C_4H_7FeCl^+$, $C_4H_6Fe^+$, $C_4H_7FeGeCl_3^+$, CO^+, Fe^+, and $C_4H_7Fe(CO)GeCl_3^+$.

The formation of 37, formally an oxidative addition reaction, possibly occurs via protonation on the butadiene ligand with concurrent attack by $GeCl_3^-$ on the

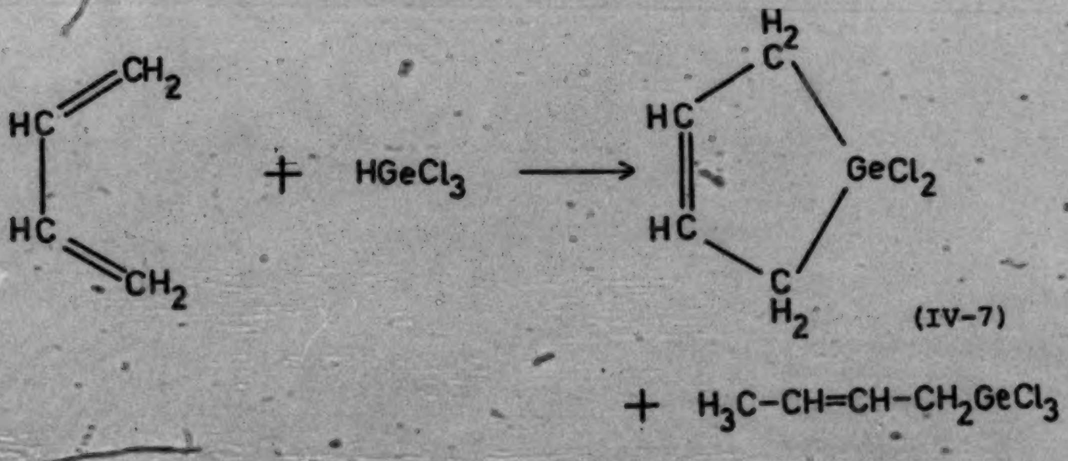


Molecular Structure of $(C_3H_5)Fe(CO)_3GeCl_3$

The Fe-Ge bond lies directly below the Fe-C(2) bond.

Figure 28

iron atom as a result of the formation of $H^+GeCl_3^-$ (see I-28). A study of the reaction between liquid 1,3-butadiene and trichlorogermane led to the isolation of two compounds:[262]



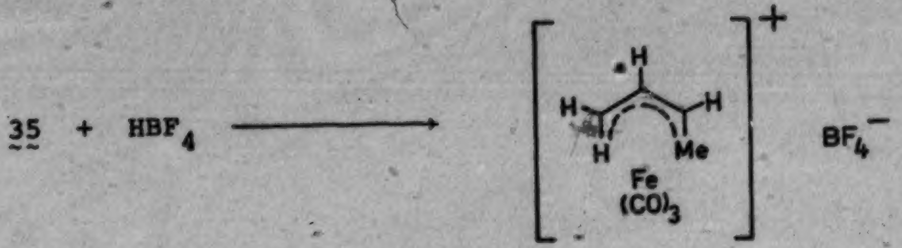
(IV-7)

The formation of the germacyclopentene complex was favoured 3:1 to 9:1 over that of the 1-trichlorogermyl-2-butene. Although the preponderance of one product does not necessarily prove that there was a large concentration of divalent $GeCl_2$ in solution, at least in this system the reaction yielded principally the insertion-type product. In contrast, it does not seem likely that the formation of 37 would occur through the extended reaction mechanism involving initial insertion of $GeCl_2$ across the 1,4-positions of the butadiene ligand, subsequent cleavage of the Ge-C bond on addition of HCl, as well as migration of an incipient $GeCl_3$ group.

It is possible that the formation may occur via addition of $HGeCl_3$ across one double bond, or across the two ends of the butadiene ligand, with subsequent migration of a $GeCl_3$ moiety. However, nmr evidence for the formation of the *anti*-1-methylallyl isomer (*vide infra*) argues against addition across one double bond.

Although at the present time one cannot rule out initial attack of a germanium moiety at the iron atom, with the formation of a germanium-iron bond prior to formation of the allyl ligand, this alternative is not thought to be as likely as initial attack on the butadiene ligand, in view of the more reactive nature of the organic group (from an electronic as well as stereochemical viewpoint).

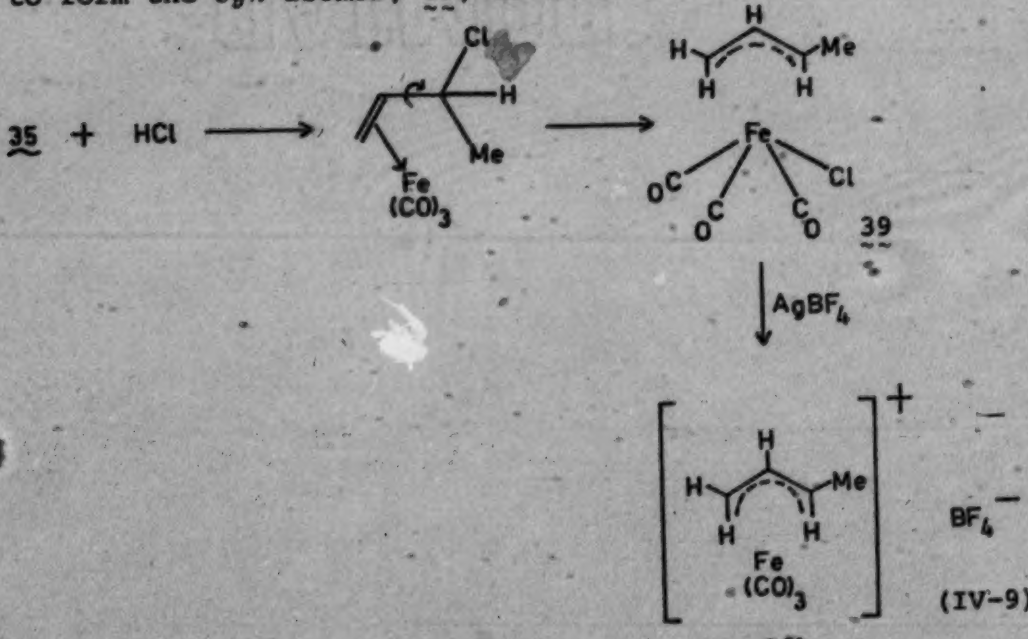
With regard to initial protonation of the butadiene ligand, it has been found that reaction of 35 with HBF_4 gives the *anti* isomer, 38a; i.e., a protonated product that preserves the configuration of the diene complex:[263]



(IV-8)

38a

The cation 38a is not the same isomer obtained from 35 by addition of HCl followed by halogen abstraction by $AgBF_4$ (38b). It was suggested that geometrical inversion must occur following *cis* addition of HCl in reaction IV-5 to form the *syn* isomer, 39, as in IV-9:[263]



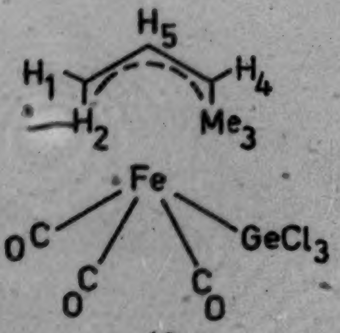
(IV-9)

38b

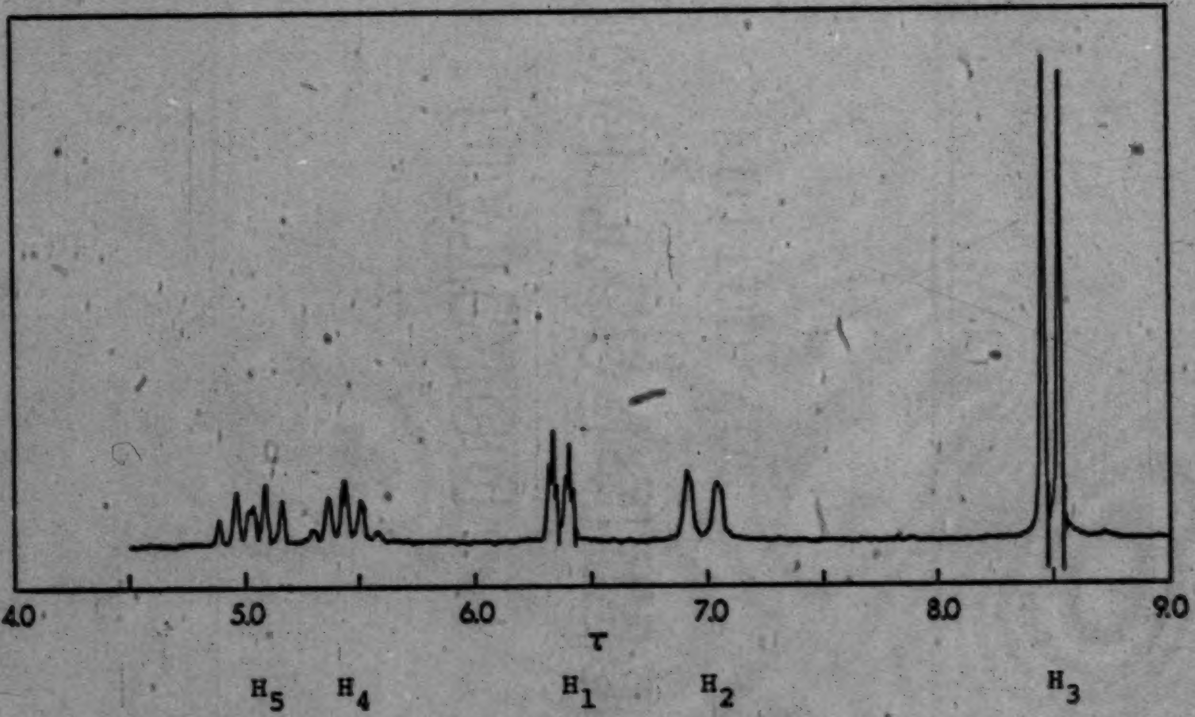
Since reaction IV-6 proceeds to afford the *anti*-1-methylallyl iron complex, i.e. without geometrical inversion, one is left with two reaction mechanisms which would preserve the configuration of the diene ligand in 35: either (1) ionization of $HGeCl_3$ to $H^+GeCl_3^-$, allowing protonation of the butadiene ligand, followed by attack of $GeCl_3^-$ on the iron atom, or (2) addition of $HGeCl_3$ across the two *ends* of the butadiene ligand followed by migration of a $GeCl_3$ group to the iron atom. This latter possibility might seem more likely in view of the non-polar nature of the solvent. Also, this mechanism would correspond to the formation of a 1-trichlorogermyl-2-butene ligand, the species formed as the minor product in reaction IV-7.

It should be noted that the mechanisms above are only suggested as extreme possibilities for this reaction, and the actual mechanism might proceed via a more complex pathway or modification of these extremes.

The assignment of an *anti* configuration for the methyl group as in 40 follows from the nmr spectrum in $CDCl_3$,



40



(*anti*-1-C_4H_7)Fe(CO)$_3$GeCl$_3$

Figure 29

which will now be discussed. The spectrum is shown in Figure 29 and chemical shifts and coupling constants are given in Table XV. With an *anti* methyl group one would expect two resonances to contain typical *cis* proton coupling constants. Referring to the numbering system in **40**, it was found from decoupling experiments that the proton at 5.43 τ is coupled to that at 6.38 τ and the methyl protons; this resonance at 5.43 τ, in a region expected for a *syn* proton, was assigned to H_4. The quintet appearance of this resonance is due to the equivalence of the H_4-methyl proton coupling constant, J_{34}, and the *cis* proton coupling constant, J_{45}. The value of 7.0 Hz is typical of three-bond *cis* couplings in olefins.[232] The other *syn* proton was assigned to the resonance at 6.38 τ, with a typical *cis* proton coupling constant, J_{15}, of 6.8 Hz. The *syn-syn* coupling constant, J_{14}, was measured as 1.5 Hz. The central proton and *anti* proton were easily assigned to the resonances centred at 5.02 and 6.98 τ, respectively. The broadened doublet at 6.98 τ (H_2) has a typical *anti* proton coupling constant of 12.0 Hz (to H_5), and is also coupled to the geminal proton, H_1 (J_{12} = 2.0 Hz).

Finally, the central proton, H_5, at 5.02 τ is a doublet of triplets, due to a large *anti* proton coupling, and two almost equivalent *syn* proton coupling constants.

D. Suggestions for Further Research

The work on allyl derivatives of $CpRe(CO)_3$ presented in this chapter provides the basis for a much broader study into these compounds. The halide derivatives, Cp(allyl)Re(CO)X, will likely be valuable starting materials for a wide variety of rhenium compounds if the anion, $[Cp(allyl)Re(CO)]^-$, can be formed by reduction of the halide with sodium amalgam, analogous to the formation of $[C_3H_5Fe(CO)_3]^-$ from $C_3H_5Fe(CO)_3Cl$.[105] Providing the anion is reasonably stable, the number of possible reactions with organic and inorganic electrophiles would be almost limitless. Besides compounds of the form Cp(allyl)Re(CO)R (R = hydrocarbon, fluorocarbon, group IV metal ligand, transition metal complex), it may also be possible to displace the carbonyl group in the anion to form, e.g., Cp(allyl)Re(NO) (from $NOPF_6$), $[Cp(allyl)-RePR_2]_2$ (from $ClPR_2$), or perhaps even $Cp(allyl)_2Re$ (from allyl halides).

Halide displacement reactions of Cp(allyl)Re(CO)X with alkali metal compounds such as $Na[CpFe(CO)_2]$, $LiER_3$ (R = alkyl or aryl group, E = Si, Ge, Sn), or RLi (R = hydrocarbon or fluorocarbon group) might also produce compounds of the form Cp(allyl)Re(CO)R. If direct halide displacement reactions are not productive, one might attempt the extraction of the halogen atom by a halide acceptor such as $AlCl_3$, in the presence of carbon monoxide, to form, e.g., $[Cp(allyl)Re(CO)_2]^+$-$[AlCl_4]^-$. Reactions of this cation with nucleophilic reagents would probably displace one carbonyl ligand to form other Cp(allyl)Re(CO)R compounds similar to those mentioned above.

Although the reaction between $Cp(2\text{-}C_4H_7)Re(CO)Cl$ and $HGeCl_3$ did not lead to the isolation of an insertion product, this does not preclude the possibility of forming other insertion products from reactants such as $SnCl_2$ or SnI_2. Allyl displacement reactions and insertion reactions into the allyl-metal bond would also be informative about the reactivity of the allyl-rhenium bond.

Concerning the hydride, $Cp(2\text{-}C_4H_7)Re(CO)H$, it would be of interest to explore the reactivity of the rhenium-hydrogen bond towards insertions using such reactants as fluoroalkenes or diazomethane. Elimination of hydrogen by reactions with group IV or V hydrides (e.g. HPR_2, HER_3, R = alkyl or aryl group, E = Si, Ge, Sn) also affords a possible route to Cp(allyl)Re(CO)R compounds. There also exists a number of possible routes to the iodide, $Cp(C_3H_5)Re(CO)I$, free from other rhenium halide compounds, by reacting $Cp(C_3H_5)Re(CO)H$ with HI, I_2, or CH_3I. The possibility of displacing the hydrogen atom and the allyl group as 2-methylpropene should also be explored.

Finally, the use of other substituted allyl halide starting materials in reactions with $CpRe(CO)_3$ would provide further information about the spectroscopic and chemical properties of allylrhenium complexes.

From the present work, a limiting factor in the exploration of the chemistry of these cyclopentadienylallylrhenium complexes would be the low yields of the preparative reactions. If the reactants or reaction conditions could be changed to significantly increase the yield of the Cp(allyl)Re(CO)X complexes, there should be no restriction to a full study of these compounds.

TABLE XV

^1H NMR DATA FOR ALLYL DERIVATIVES[a]

Compound	Chemical Shifts (τ)						
	Cp	H_1	H_2	H_3	H_4	H_5	H_6
$Cp(C_3H_5)Re(CO)Cl^b$	4.61	7.00	7.65	6.43	7.00	5.50	
$Cp(C_3H_5)Re(CO)Br^c$	4.61	6.99	7.75	6.54	6.70	5.63	
$Cp(2\text{-}C_4H_7)Re(CO)Cl^b$	4.64	7.21	7.51	6.22	6.97	7.32	
$Cp(2\text{-}C_4H_7)Re(CO)H^c$	4.85	7.07	8.17	7.95	7.54	7.65	21.94
$(1\text{-}C_4H_7)Fe(CO)_3GeCl_3{}^{b,d}$		6.38	6.98	8.49	5.43	5.02	

Compound	Coupling Constants (Hz)									
	J_{15}	J_{25}	J_{35}	J_{45}	J_{14}	J_{12}	J_{23}	J_{24}	J_{34}	J_{16}
$Cp(C_3H_5)Re(CO)Cl^b$	~5.0	7.3	10.1	~5.0			0.9			
$Cp(C_3H_5)Re(CO)Br^c$	5.5	8.0	9.6	6.0	3.4	1.2	0.9	0.6		
$Cp(2\text{-}C_4H_7)Re(CO)Cl^b$					3.9	1.2				
$Cp(2\text{-}C_4H_7)Re(CO)H^c$					3.4	e	e	e	e	2.8
$(1\text{-}C_4H_7)Fe(CO)_3GeCl_3{}^{b,d}$	6.8	12.0		7.0	1.5	2.0			7.0	

TABLE XV (continued)

[a] TMS as internal reference; peak integrals were consistent with the formulations.

[b] In $CDCl_3$ at ambient temperature.

[c] In CD_2Cl_2 at ambient temperature.

[d] $CHCl_3$ as internal reference for decoupling experiments.

[e] Observed but not measurable.

TABLE XVI

INFRARED AND RAMAN SPECTRA OF ALLYL DERIVATIVES[a]

Compound	Type	Stretching Frequencies, cm^{-1}	
		ν(M-H)	ν(C≡O)
$Cp(C_3H_5)Re(CO)Cl$	infrared		1981(s)
$Cp(C_3H_5)Re(CO)Br$	infrared		1980(s)
$Cp(C_3H_5)Re(CO)I$[b]	infrared		1975(s)
$Cp(2\text{-}C_4H_7)Re(CO)Cl$	infrared		1973(s)
$Cp(2\text{-}C_4H_7)Re(CO)H$	infrared	1984(vw)	1924(s)[c]
$Cp(2\text{-}C_4H_7)Re(CO)H$	Raman	1985(w,br)	1923(m)
$(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$	infrared		2079(vs) 2029(s) 2024(s)

[a] In heptane; abbreviations as in Table II.

[b] Characterized by infrared and mass spectrometry only.

[c] $\nu(^{13}C{\equiv}O)$ 1877(w).

TABLE XVII

PHYSICAL DATA, YIELDS, AND REACTION TIMES FOR ALLYL DERIVATIVES

Compound	Colour	Reaction time, hours	Yield, %	Mp, °C	Calculated %			Found %		
					C	H	X^b	C	H	X^b
$Cp(C_3H_5)Re(CO)Cl$	yellow	8	10	dec. >110	30.4	2.83	9.96	30.6	3.10	10.74
$Cp(C_3H_5)Re(CO)Br$	yellow	2.5	14	dec. >90	27.0	2.52	20.0	27.3	2.49	20.3
$Cp(2\text{-}C_4H_7)Re(CO)Cl$	yellow	1	41	128-130	32.5	3.27	9.59	32.6	3.36	9.90
$Cp(2\text{-}C_4H_7)Re(CO)H$	white	1	40	28-29	35.8	3.91		36.0	3.93	
$(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$[a]	yellow	2	80	81-83	22.5	1.89	28.4	22.6	1.83	27.9

[a] Osmometric molecular weight in acetone: calculated, 374; found, 370.

[b] X = Cl or Br.

EXPERIMENTAL

GENERAL TECHNIQUES AND MATERIALS

As described in previous chapters, a nitrogen atmosphere was maintained during all reactions and workup procedures. Ultraviolet irradiations were carried out with the 450 watt Hanovia lamp at about room temperature.

Melting points, microanalyses, infrared, and mass spectra were obtained as previously described. All nmr spectra were obtained on a Varian Model HA-100 spectrometer.

Solvents were distilled from drying agents under nitrogen as before. The following chemicals were obtained from commercial sources as noted: allyl chloride and methylallyl chloride from Eastman Kodak Co., Rochester, N.Y.; allyl bromide from The British Drug Houses, Ltd., Poole, England; allyl cyanide from Peninsular ChemResearch, Inc., Gainesville, Fla.; butadiene iron tricarbonyl from Strem Chemicals, Inc., Danvers, Mass.; and silver hexafluorophosphate from Ozark-Mahoning Company, Tulsa, Okla.

Cyclopentadienylrheniumtricarbonyl was prepared as previously described. Allyltrimethyltin (kindly supplied by Dr. J. Jeffery) was prepared according to the method of Abel and Moorhouse.[233]

PROCEDURES

Synthesis of Cp(allyl)Re(CO)X

The same general procedure was used for the allyl chloride, allyl bromide, and methylallyl chloride derivatives. A solution of $CpRe(CO)_3$ (1.0 g, 3.0 mmol) and the allyl halide (30 mmol) in 200 ml cyclohexane was irradiated with the 450 watt source until the concentration of the product relative to that of unreacted $CpRe(CO)_3$ seemed to be the greatest (for reaction times, see Table XVII). The reaction solution was concentrated on a rotary evaporator to about 10 ml, and chromatographed on either Florisil or silicic acid. Elution with a 1:1 mixture of petroleum ether: dichloromethane removed all unreacted starting materials, and subsequent elution with dichloromethane gave a yellow solution of the product. Addition of 50 ml heptane to this solution and concentration of the solution on a rotary evaporator initiated crystallization, affording large yellow crystals of product. Yields are given in Table XVII.

Reaction Between Allyl Iodide and $CpRe(CO)_3$

A solution of $CpRe(CO)_3$ (1.0 g, 3.0 mmol) and C_3H_5I (2.7 ml, 30 mmol) in 200 ml cyclohexane was irradiated with the 450 watt source for ten hours. The reaction solution was concentrated to about 10 ml and chromatographed on Florisil. A broad red band, eluted with mixtures of petroleum ether:dichloromethane varying from

1:1 to 1:5, was collected in five fractions. All fractions contained predominantly *trans*-$CpRe(CO)_2I_2$, as shown by infrared spectra, except the third fraction, which showed approximately twice as much of the allyl complex as of the diiodide. The amount of material in the third fraction did not warrant further chromatography, and crystallization afforded a material containing the same ratio of products. The amount of *trans*-$CpRe(CO)_2I_2$ obtained from the other fractions totalled 0.89 g (53%), analytically pure after recrystallization from dichloromethane-heptane.

Synthesis of $Cp(2\text{-}C_4H_7)Re(CO)H$

A yellow solution of $Cp(2\text{-}C_4H_7)Re(CO)Cl$ (0.61 g, 1.7 mmol) and $LiAlH_4$ (0.30 g, 8.0 mmol) in 100 ml THF, previously distilled from sodium/benzophenone, was refluxed for one hour. The solution became very pale yellow-green, and after cooling, the THF was removed on a vacuum line. After addition of 150 ml warm heptane, the solution was filtered through a small amount of Celite and the heptane was removed on a vacuum line. From the pale green oily residue, hard white crystals formed on a water-cooled cold finger during overnight sublimation at 60° *in vacuo*. The yield of $Cp(2\text{-}C_4H_7)Re(CO)H$ was 0.22 g (40%). Spectroscopic and analytical data were obtained without further purification.

Synthesis of $(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$

A solution of (1,3-butadiene)$Fe(CO)_3$ (0.39 g, 2.0 mmol) and $HGeCl_3$ (0.90 g, 5.0 mmol) in 80 ml petroleum ether was stirred magnetically for two hours. A yellow oil formed on the bottom of the reaction vessel. Dichloromethane was added to just dissolve the oil, and the solution was cooled to -20°, affording 0.28 g of yellow crystals. The mother liquor was concentrated and cooled again, affording two more crops of crystals. Total yield of $(1\text{-}C_4H_7)Fe(CO)_3GeCl_3$ was 0.60 g (80%). An analytical sample was prepared by recrystallizing from warm heptane.

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